DOCTOR OF PHILOSOPHY

Evaluation of Cement and other Constituents in Historically-Significant Concrete Structures in Scotland

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EVALUATION OF CEMENT AND OTHER CONSTITUENTS IN HISTORICALLY-SIGNIFICANT CONCRETE STRUCTURES IN SCOTLAND

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Simeon Wilkie
April 2018

DECLARATION

I hereby declare that I am the author of this thesis, that I have consulted all of the cited references, that, unless otherwise stated, I have performed all of the reported work and that the work has not been previously accepted for a higher degree.

Simeon Wilkie

April 2018

CERTIFICATION

This is to certify that Simeon Wilkie has undertaken his research under my supervision, and that he has fulfilled the conditions of relevant Ordinance of the University of Dundee, so that he is qualified to submit the following thesis in application for the degree of Doctor of Philosophy.

Dr. Thomas Dyer
April 2018

ABSTRACT

The number of listed concrete structures in Scotland is ever increasing and, as these structures age, there is a growing need for their conservation and repair.

When repairing concrete structures it is critical to match the properties of the original material as closely as possible. Failure to match the mechanical and chemical properties can not only lead to an unsuccessful repair, but can also cause significant damage and accelerated deterioration to the original material. While some conservators value an 'honest' and visible repair, others feel it is important to match the aesthetic characteristics, as this will allow the two materials to blend well visually, retaining the historic character of the structure. However, in order to match these properties it is first necessary to determine both the chemical composition and proportions of the mix constituents.

At present, there is very limited data regarding the nature of Portland cement and other constituents in historically-significant concrete structures in the United Kingdom, and that which is available covers a wide geographical area. As the properties of Portland cement and concrete are significantly influenced by the local raw materials and manufacturing processes used in their production, this data does not accurately reflect the nature of early cement and concrete compositions in Scotland.

This project aims to resolve such issues by developing a database relating the compositions of cement in concrete structures throughout Scotland to their date, architectural type, production source and physical characteristics, ultimately providing information on past practices and technologies to build up an in-depth understanding of the history of Scottish concrete.

Furthermore, there is currently a lack of clear technical guidance or specification with regards to the analysis and repair of historic concrete structures, and the existing standards for analysing hardened concrete are neither accurate nor suitable for use with chemically or physically damaged historic concrete. As such, this thesis discusses the limitations of current analysis methods and questions the extent to which it is possible to accurately evaluate historic concrete using existing methods.

1 INTRODUCTION

1.1 PROJECT BACKGROUND

The number of listed concrete structures in Scotland is ever increasing and, as these structures age, there is a growing need for their conservation and repair. The historical significance of these structures is determined by the Secretary of State, who, adhering to the Principles of Selection for Listing Buildings (Department for Culture, Media and Sport, 2010), applies the following criteria when assessing whether a building is of special interest and should be added to the statutory list:

> *Architectural Interest. To be of special architectural interest a building must be of importance in its architectural design, decoration or craftsmanship; special interest may also apply to nationally important examples of particular building types and techniques (e.g. buildings displaying technological innovation or virtuosity) and significant plan forms;*
>
> *Historic Interest. To be of special historic interest a building must illustrate important aspects of the nation's social, economic, cultural, or military history and/or have close historical associations with nationally important people. There should normally be some quality of interest in the physical fabric of the building itself to justify the statutory protection afforded by listing.*

There are over 260 sites in Scotland which feature structures containing early concrete architecture (Urquhart, 2013) and many of these historically-significant structures are in the care of Historic Environment Scotland – previously 'Historic Scotland' – who have implemented the Stirling Charter (Historic Scotland, 2000) in their approach to stewardship. The Charter outlines broad principles for the conservation of Scotland's built heritage through six key articles, aiming to ensure it is sustainably maintained for present and future generations. In line with these principles, Historic Environment Scotland is

committed to retaining the historic and architectural character of the buildings in their care during any conservation practice. This means that compatible materials and construction techniques must be used in repairs, and any new developments must be sensitive to the historic character of the structure (Historic Scotland, 2002).

In regards to repairing concrete structures, it is critical to match the properties of the original material as closely as possible. Failure to match the inherent mechanical and chemical properties may not only lead to an unsuccessful repair but can also cause significant damage and accelerated deterioration of the original material, as the repair material can induce stresses on the surrounding area due to the differences in these properties. It is also important to match the aesthetic characteristics, in order to allow the two materials to match well visually, retaining the historic character of the structure.

However, there is very limited data regarding the nature of Portland cement and other constituents in historically-significant concrete structures in the United Kingdom, and that which is available covers a wide geographical area. As the properties of these materials are significantly influenced by the local raw materials and manufacturing processes used in their production, this data does not accurately reflect the nature of early cement and concrete compositions in Scotland.

1.2 PROJECT AIMS AND OBJECTIVES

This project aims to address these issues by providing information on past practices and technologies and building an in-depth understanding of the history of Scottish concrete. This information can then be disseminated by Historic Environment Scotland and the University of Dundee to conservators, building owners and other interested parties, to aid them in their approach to the conservation of concrete structures and cementitious materials.

The project intends to achieve this by completing the following objectives:

1. Review literature relating to the past practices and technologies of cement manufacture and concrete construction;
2. Establish a method of best practice for the analysis and repair of historically-significant concrete structures;
3. Review historic test data relating to concrete structures in Scotland which pre-date 1950;

4. Analyse samples of cementitious renders, mortar and concrete from structures across Scotland which pre-date 1950;
5. Develop a database that relates the composition of cements in structures throughout Scotland to their age, architectural type, production source, and physical characteristics.

1.3 THESIS OUTLINE AND SCOPE OF STUDY

1.3.1 Chapter 2: Literature Review

Concrete has developed significantly over several thousand years to become the material that it is used today. This chapter aims to give an overview of these developments and highlight the most significant.

Furthermore, as this project aims to inform readers from a variety of different technical backgrounds, this chapter builds a foundational knowledge of Portland cement chemistry, the deterioration mechanisms of concrete, methods of concrete repair, and the material characteristics which must be considered in order to achieve a successful repair – all of which are essential to fully understand the context of the subsequent chapters.

1.3.2 Chapter 3: Methodology

A wide variety of physical, chemical and statistical analysis techniques have been applied in this project in order to characterise historic concrete samples. This chapter details the methods and principles to which these were carried out, as well as the specific materials and equipment that were used to carry out all testing procedures.

1.3.3 Chapter 4: Control Study

At present, there is a lack of standards regarding the forensic analysis of historic concrete. As such, existing British standards – which are not intended for this purpose – are commonly applied in the forensic analysis of historic concrete. In this chapter, a review of these standards is undertaken as part of a control study to determine their suitability for use in this field.

In order to fully assess the limitations of the current standards when used in the analysis of historic concrete samples, nine concrete mixes were produced using Portland cement (CEM I 42.5N) as the sole cement constituent, and with mix proportions based on typical mix designs from the early 20th century. These proportions were approximately 1:1:2, 1:2:4 and 1:1.5:3 by mass of cement, sand and coarse aggregate respectively, but with the

sand content slightly adjusted for each mix in order to maintain a constant cement and coarse aggregate content per 1 m^3 while varying the w/c ratio.

The concrete was cast in 100x100x500 mm moulds, and slices of approximately 100x100x15 mm were then taken from the centre of each concrete sample after curing for 28 days and placed in a carbonation tank at 4% CO_2 for fourteen weeks in order to simulate the carbonation that would have occurred naturally in historic concrete.

These samples were then analysed following BS 1881-124 (British Standards Institution, 2015a), with the exception of density tests which were carried out in accordance with BS EN 12390-7 (British Standards Institution, 2009a), aggregate water absorption tests which were carried out in accordance with BS EN 1097-6 (British Standards Institution, 2013b), and chemically-bound water prior to carbonation, which was estimated using XRF analysis combined with an optimisation process which determined the percentage of chemically bound water by mass of anhydrous cement required to achieve full hydration. The results from these analyses were then used to estimate the original mix proportions, and this estimation compared to the actual mix proportions in order to determine whether these techniques can be used to accurately assess concrete of unknown mix proportions with the objective of creating 'like-for-like' replacements.

1.3.4 Chapter 5: Review of Historic Test Data

Restrictions preventing the removal of material from historically-significant structures has made it difficult to obtain samples for forensic analysis. Therefore, a review of pre-existing test data was carried out in order to better understand the historic changes that have occurred in the design and manufacture of concrete in structures across Scotland.

Pre-existing reports of the analyses of 119 samples from 36 structures pre-dating 1950 were reviewed. These reports included visual analyses of concrete cores, the degree of carbonation, chemical analyses, compressive strength and density at various saturation states.

The laboratory test data from each of these samples was recorded and, in combination with further data from 90 *in-situ* covermeter surveys previously carried out across these structures, analysed in order to try and establish a greater understanding of historic concrete construction in Scotland. These results were also compared with modern design codes, in order to present them in context with the current understanding of concrete durability and the related design criteria.

Cover to reinforcement, compressive strength, hardened density and chemical analyses were determined in accordance with BS 1884-204 (British Standards Institution, 1988a), BS 1881-120 (British Standards Institution, 1983a), BS 1181-114 (British Standards Institution, 1983b), BS 1181-124 (British Standards Institution, 1988b) and BS 4551 (British Standards Institution, 1980) respectively.

1.3.5 Chapter 6: Historic Sample Study

Historic samples obtained from locations across Scotland were analysed to determine their physical and chemical characteristics, and to establish the differences in Portland cement and other constituents that exist as a result of changes in manufacturing technology and processes over time, available raw materials, and the introduction of material standards and design legislation.

The samples used in this study included varying types of concrete which were cast *in-situ* (reinforced, mass, lightweight), precast concrete, mortar and render – all of which had a Portland cement binder. The analyses included chemical and mineralogical compositions, aggregate content and particle size distribution, and LOI (loss-on-ignition).

Additionally, a study of the drying shrinkage properties of 24 of the samples was undertaken and a statistical analysis of the results performed in order to determine which physical properties had the most influence on drying shrinkage, and their implications on the conservation of historically-significant concrete structures.

1.3.6 Chapter 7: Conclusion

The final chapter of this thesis summarises the previous chapter conclusions and discusses the implications that these pose for the conservation of historically-significant concrete structures when considered together. Additionally, this chapter discusses the inadequacy of current analysis methods and the recommendations for future work in this field.

2 LITERATURE REVIEW

2.1 HISTORIC CONCRETE DEVELOPMENTS

For thousands of years, concrete, in one form or another, has been a key construction material in many cultures throughout the world. Over this time there have been many developments in concrete technology which have significantly altered its composition, manufacture and subsequent practical applications, leading to it becoming the most widely used construction material in the world today; annual global production reached approximately 13 billion metric tons in 2007 (Aïtcin & Mindess, 2011), with a value of approximately 2,400 billion USD (Jahren & Sui, 2013).

BS ISO 6707-1 (British Standards Institution, 2014a) defines concrete as a *"mixture of aggregate, cement and water, which hardens,"* and cement as *"finely ground inorganic material that, when mixed with water, forms a paste that sets by means of hydration reactions processes, and that, after hardening, retains its strength and stability, even underwater."* However, as the composition and manufacturing process of concrete has evolved over such a long period of time, the term 'concrete' is often used to describe an extensive range of cast artificial stone which consist of aggregate and binder – both of which vary greatly as a result of changes in the available materials and technology.

Aggregate, which can include an assortment of sand, gravel and crushed rock, has historically been dependent on the local geology and the technology available to crush rock into a particular size. As a result of this, the composition and size-grading of aggregate in historic concrete can be extremely variable, which has a significant impact on the properties and practical applications of both fresh and hardened concrete.

Like aggregate, the composition and subsequent properties of the binder are also dependent on the local geology, as this supplies the raw materials required to create a binder – leading to significant variations in binder between production locations. The

degree of thermal decomposition is also an important factor which affects the properties of the binder and this has subsequently been affected by advancements in kiln technology and the ability to treat the materials at a higher temperature.

As the different varieties and combinations of constituent materials have a significant effect on the properties of the final hardened material, it is important to have clarity in the definitions of these. Table 2-1 contains the classifications of lime terms as found in BS EN 459-1 (2015b), while Table 2-2 contains the classifications of material terms as found in BS ISO 6701-1 (2014a), BS 6100-9 (2007) and BS EN 459-1 (2015b).

Table 2-1 – Classification of limes

TERM	DEFINITION
Building lime	Group of lime products, exclusively consisting of two families: air lime and lime with hydraulic properties, used in applications or materials for construction, building and civil engineering
Air lime	Lime which combines and hardens with carbon dioxide present in air. Air lime has no hydraulic properties. Air lime is divided into two sub-families, calcium lime (CL) and dolomitic lime (DL)
Calcium lime	Calcium lime is an air lime consisting mainly of calcium oxide and/or calcium hydroxide without any hydraulic or pozzolanic addition.
Dolomitic lime	Dolomitic lime is an air lime consisting mainly of calcium magnesium oxide and/or calcium magnesium hydroxide without any hydraulic or pozzolanic addition.
Quicklime	Quicklime is an air lime mainly in the oxide form which reacts exothermically on contact with water
Hydrated lime	Hydrated lime is an air lime mainly in the hydroxide form produced by the controlled slaking of quicklime
Lime with hydraulic properties	Building lime consisting mainly of calcium hydroxide, calcium silicates and calcium aluminates. It has the property of setting and hardening when mixed with water and/or under water. Reaction with atmospheric carbon dioxide is part of the hardening process. Lime with hydraulic properties is divided into three subfamilies, natural hydraulic lime (NHL), formulated lime (FL) and hydraulic lime (HL)
Natural hydraulic lime	Natural hydraulic lime is a lime with hydraulic properties produced by burning of more or less argillaceous or siliceous limestones (including chalk) with reduction to powder by slaking with or without grinding. It has the property of setting and hardening when mixed with water and by reaction with carbon dioxide from the air (carbonation)
Formulated lime	Formulated lime is a lime with hydraulic properties mainly consisting of air lime (CL) and/or natural hydraulic lime (NHL) with added hydraulic and/or pozzolanic material. It has the property of setting and hardening when mixed with water and by reaction with carbon dioxide from the air (carbonation)
Hydraulic lime	Hydraulic lime is a binder consisting of lime and other materials such as cement, blast furnace slag, fly ash, limestone filler and other suitable materials. It has the property of setting and hardening under water. Atmospheric carbon dioxide contributes to the hardening process

Source: Original definitions from BS EN 459-1 (British Standards Institution, 2015b)

Table 2-2 – Classification of material terms

TERM	DEFINITION	STANDARD
Binder	Material used to hold solid particles together in a coherent mass	BS ISO 6707-1
Concrete	Mixture of aggregate, cement and water, which hardens	BS ISO 6707-1
Cement	Finely ground inorganic material that, when mixed with water, forms a paste that sets by means of hydration reactions processes, and that, after hardening, retains its strength and stability, even underwater	BS ISO 6707-1
Aggregate	Inert granular material	BS ISO 6707-1
Mortar	Mixture of binder, fine aggregate and water, which is normally used as a jointing material	BS ISO 6707-1
Render	Mixture of one or more inorganic binders, aggregate, water and, sometimes, admixtures, used to obtain an external finish	BS ISO 6707-1
Gypsum	Calcium sulfate in its fully hydrated phase	BS ISO 6707-1
Asphalt	Dense mixture of mineral aggregate and bituminous binder	BS ISO 6707-1
Bitumen	Viscous liquid of solid consisting essentially of hydrocarbons and their derivatives, soluble in trichloroethylene and which is substantially non-volatile and softens gradually when heated	BS ISO 6707-1
Latent hydraulic material	Hydraulic material that acts by the addition of an activator	BS 6100-9
Blended hydraulic cement	Mixture of cement and latent hydraulic material	BS 6100-9
Clinker	Solid material formed in high-temperature processes by total or partial fusion	BS 6100-9
Portland cement	Cement based on ground Portland cement clinker	BS 6100-9
Portland cement clinker	Clinker formed from a predetermined homogeneous mixture of materials comprising lime silica, a small proportion of alumina and generally iron oxide	BS 6100-9
Pozzolana	Latent hydraulic material that contains siliceous or siliceous and aluminous materials	BS 6100-9
Pozzolanicity	Ability of a material to combine with calcium hydroxide at ambient temperatures and in the presence of water in order to produce compounds having the properties of a cement	BS 6100-9
Lime	Calcium oxide and/or hydroxide, and calcium-magnesium oxide and/or hydroxide produced by the thermal decomposition (calcination) of naturally occurring calcium carbonate (for example limestone, chalk, shells) or naturally occurring calcium magnesium carbonate (for example dolomitic limestone, dolomite)	BS EN 459-1

It should be noted that, while the classification of limes can be found in Table 2-1, this research project is focused solely on historic Portland cement and not on building lime. Nevertheless, it is still important to have a detailed understanding of the different lime products at this stage, as the historic use of building lime played a crucial role in the development of early Portland cement, and there can be some confusion in differentiating between the two.

2.1.1 Ancient Beginnings

While it is unclear when concrete was first made, or even where it first originated, it is likely that attempts to make it occurred at several different and unrelated locations during the Neolithic era.

The oldest known concrete was discovered in 1985 at Yiftah El in Southern Galilee, Israel and dates to around 7000 BCE (British Cement Association, 1999). This early lime concrete, produced from a mixture of quicklime, water and stone, was laid on an even base of sandy clay to form a 180m^2 floor that varied in thickness between 30 and 80 mm. The fragmented remains of what was probably a limestone-burning kiln lining were also discovered at the site.

Another ancient concrete discovery was made at Lepenski Vir, in what is now Serbia, where a red lime concrete was used to make hut floors. Lepenski Vir lies on the banks of the Danube, and the red lime was brought from almost 200 miles upstream, suggesting its users had some knowledge of its properties, and mixed with sand, gravel and water to produce concrete (Stanley, 1979). This concrete, which dates to around 5600 BCE, was laid and compacted to form a 250 mm thick floor which incorporated a stone hearth at one end.

By 5000 BCE the art of concrete making appears to have died out and it is not until around 2500 BCE, in Ancient Egypt, that evidence of concrete use can again be found. Although it was only moist mud that was used as mortar between sun-dried bricks (Davey, 1961) in most Egyptian construction at this time, cementitious material and concrete were incorporated into larger, monumental structures such as the Great Pyramid of Giza. While some authors believe this material was lime-based, many agree that it was more likely to have been produced from burnt gypsum (Stanley, 1979; Davey, 1961; Blezard, 1998; British Cement Association, 1999). The concrete works in ancient Egypt can be seen in a mural in Thebes, dating from around 1950 BCE, which depicts various stages in the

process of manufacture and application of mortar and concrete (British Cement Association, 1999).

Different sources of mortar have also been used extensively throughout the Middle East for thousands of years. While even today the ancient mortar of clay or mud, sometimes mixed with chopped straw or reeds, is used across the Middle East, evidence suggests that gypsum and asphaltic mortars have been used for bedding burnt bricks from as early as the third millennium BCE (Davey, 1961). The remains of a lime-kiln in Mesopotamia suggest that lime-burning was practiced there from at least as early as 2450 BCE, and that the asphaltic mixtures used in construction were largely replaced by mixtures of hydrated lime, clay, bitumen, ashes and other materials in the time of Nebuchadnezzar's rule over Babylon (Davey, 1961).

By 500 BCE concrete and cement were also being used in Ancient Greece with a relatively high degree of skill and with knowledge of the effects of highly siliceous, volcanic Santorin earth which started to be used as cement sometime between 500-300 BCE (Idorn, 1997). Evidence of the Ancient Greek skill and knowledge of concrete was discovered during the archaeological excavation of the ancient city of Kamiros on the island of Rhodes, where a great water-storage tank with a capacity of $600m^2$ was unearthed close to the temple of Athena of Kamiros (Koui & Ftikos, 1998). The concrete used in the water tank construction combined a mixture of siliceous gravel, granular intermediate calcareous aggregates and fine-grained aggregates with a natural cement binder, consisting of volcanic earth and lime; forming a concrete of such high quality that it was found to have excellent physical and mechanical properties, despite three millennia of weathering (Koui & Ftikos, 1998). The Ancient Greeks also made use of lime-based compositions as a render for porous limestone used in temples, as a binding material between bricks and stone, and to cover walls of sun-dried bricks – as reported of the palaces of Croesus and Attalus (British Cement Association, 1999).

2.1.2 Roman Innovation

The word 'concrete' comes from the Latin 'concretus' meaning 'grown together' or 'compounded' (Stanley, 1979), and perhaps the most significant period in the history of concrete began at around 300 BCE when the Romans began to develop and use concrete for ambitious construction projects. One of their earliest uses of concrete was in foundations – such as those in the podia of the temples of Castor (117 BCE) and Concord (121 BCE) (Davey, 1961).

At some point in the second century BCE, Roman builders began to use a pink volcanic ash containing silica and alumina, quarried from several different places around the Bay of Naples; mixing it with lime as they believed it to be sand. The Romans discovered that this mixture resulted in a much stronger concrete than anything they had been able to previously produce (Stanley, 1979). The best source of this volcanic material was found to come from Pozzuoli and, as a result of this, the material became known as pozzolana (Blezard, 1998) – a material which would significantly alter the future of concrete construction. Vitruvius described it as "*a kind of powder which from natural causes produces astonishing results*," and wrote that "*This substance, when mixed with lime and rubble, not only lends strength to buildings of other kinds, but even when piers of it are constructed in the sea, they set hard under water*," (Vitruvius & Morgan, 1914).

It is possible that this pozzolana was first used at Puteoli and Cosa, north of Rome, to make hydraulic mortar for marine concrete (Idorn, 1997), and later used in large-scale projects such as the theatre in Pompeii, constructed in 75 BCE, where concrete was used as an infill material in walls with a stone or brick facade (British Cement Association, 1999). When Rome was reconstructed in the first century AD, pozzolana concrete was widely used (Newby, 2001), and many of those concrete structures are still in existence today. In areas where pozzolana was not available, Roman builders would instead crush tiles or pottery into a powder and add this to their cement to produce a similar effect (Blezard, 1998).

While the development of pozzolanic concrete was a great achievement, the Romans also experimented with other concrete construction techniques which, while less enduring than pozzolanic concrete, certainly show no less ingenuity and forward thinking. For instance, Roman builders attempted to reinforce some of their structures with bronze strips and rods (Stanley, 1979) which, despite some improvement in tensile strength, proved unsuccessful as the difference in rates of thermal expansion between the bronze and concrete lead to spalling and cracking.

This meant that concrete structures had to be designed in such a way that load was carried in compression, resulting in walls of massive thickness – sometimes in excess of 8 metres (Stanley, 1979). Consequently, lightweight concrete was developed to reduce the need for such massive buttresses and walls (British Cement Association, 1999), with early attempts made by casting large earthenware jars into walls and arches, and later by introducing crushed pumice, a porous volcanic rock, as a lightweight aggregate (Stanley,

1979). Lightweight concrete was subsequently used in two of the most prestigious and notable Roman constructions; the Colosseum, completed in 82 AD, and the Pantheon, completed in 127 AD – both of which have endured to the present as a testament to Roman engineering.

The Colosseum, an oval 190 by 130 metres, was the largest of Rome's amphitheatre with seating capacity for 50,000 spectators. It has foundations made of dense concrete, but arches and vaults constructed of lightweight concrete, which have survived despite lightning strikes, earthquakes and vandalism (British Cement Association, 1999). The Pantheon was one of the few buildings in Rome to have survived intact after the fall of the Roman Empire. Its unique domed roof is 43.4 metres in diameter (Newby, 2001) and is constructed from lightweight concrete in which crushed pumice was used as an aggregate (Stanley, 1979). At the time the dome was three times larger than any other built (Newby, 2001) and remained the largest in the world until the 20th Century (British Cement Association, 1999).

As the Roman Empire expanded, Roman engineers carried their knowledge of cement and concrete with them. Due to the difficulty of transporting pozzolana from Rome, most of the Roman concrete used in Britain was a lime concrete, making use of the local material which was available (Stanley, 1979); although ground tiles were sometimes added to produce a higher quality material (Blezard, 1998). Perhaps the most significant Roman construction in Britain is Hadrian's Wall (122-130 AD), a 3m high stone and concrete wall which stretched 120km from the Solway Firth to Tyne and included 16 forts – each housing 500 to 800 men, 80 small forts and 158 towers (Stanley, 1979).

Following the fall of the Roman Empire, it appears that most of the Roman knowledge and skill regarding concrete construction and pozzolanic materials disappeared completely (Stanley, 1979). Despite being recorded by authors such as Vitruvius, the fact that it was written in Latin and most people had limited access to these records meant that this knowledge was largely confined to the Catholic Church (Idorn, 1997).

While the use of concrete seems to have died out at this time, lime continued to be used with a high degree of skill and knowledge. During the Renaissance period, Italian architect Leon Battista Alberti wrote about the use of building materials in his books, the compilation of which can be found in the English translation, '*The Architecture of Leon Batista Alberti in Ten Books'* (Alberti, 1755). In these writings, Alberti dedicates a whole chapter to lime and plaster of Paris, in which he describes the nature of lime, its

uses and kinds, and comments that *"The lime commended by the best judges, is that which loses a third part of its weight by burning"*. Alberti goes on to discuss, not only the most suitable type of lime for different types of stonework, but also the methods of preparing and burning the lime.

2.1.3 The Development of Hydraulic Cements

2.1.3.1 Eddystone Lighthouse

In 1756 John Smeaton received a commission to build what would be the third Eddystone Lighthouse on the Eddystone Rocks in the English Channel. The two previous lighthouses had been made of timber and, as one of these had burned down and the other had blown away, Smeaton realised that the only practical solution was to construct a tower of stone blocks cemented together. This method presented its own problem as the only cements available at the time were weak and slow-setting, allowing them to be washed away before hardening (Stanley, 1979). As such, Smeaton searched for a suitable mortar and, after reading the work of Vitruvius and Bélidor, carried out a series of tests to determine what it was that made some limes, tarras and pozzolans hydraulic – establishing it was the clay content that imparted this property (Newby, 2001).

Ultimately a thoroughly mixed mortar, of equal parts Blue Lias hydraulic lime from South Wales and Italian pozzolana from Civita Vecchia, was used for the work and the lighthouse completed in 1759 (Blezard, 1998). Smeaton went on to carry out further research into the production of hydraulic limes and cement, which, along with his original research, was published in his 1791 book (Newby, 2001), *'A Narrative of the Eddystone Lighthouse'*.

Smeaton was not the only researcher at that time with an interest in the effects of pozzolanic material, and in 1778 French geologist M. Faujas de Saint-Fond published a thorough study of pozzolanic materials, their properties and effects. Despite referencing the Swedish production of pozzolana used in the Troldhättan lock, there was no mention of the work carried out by Smeaton for the Eddystone Lighthouse, which was perhaps a result of the limited international interaction at that time (Idorn, 1997), or possibly due to the secretive nature of hydraulic cement development which was seen as a vital military secret for the advancement of naval harbours, and was consequently the object of much French espionage (Addis & Bussell, 2003).

2.1.3.2 Roman Cement

As the end of the eighteenth century drew near, there was a great increase in the scale of civil engineering work required for the development of canals, harbours and bridges, which in turn prompted a demand for reliable hydraulic cement (Hudson, 1972). The London Building Act of 1774 also furthered this need as it virtually prohibited the use of exposed timber details on buildings (Davey, 1961), resulting in many attempts to develop new types of cement, of which James Parker's 'Roman cement' is probably the most widely known.

While out walking on a beach on the Isle of Sheppey, Parker came across some stones, one of which he later threw into his fire at home. When the stone rolled out of the fire – thoroughly calcined – it sparked his interest and led to his experimentation and development of what would become Roman cement – named so because Parker believed he had found the key to making cement as the Romans had (Stanley, 1979). The cement stones that Parker had found were nodules of argillaceous limestone, called 'septaria', derived from the Tertiary clay beds of the London clay cliffs, and could be found lying along the foreshore of the Thames Estuary as a result of coastal erosion (Davey, 1961). The septaria contained lime, silica and alumina (Stanley, 1979), and in his 1796 patent for Roman cement, Parker described his manufacture process (Hudson, 1972):

> *The stones of clay or noddles of clay are first broken into small fragments, then burnt in a kiln, or furnace (as lime is commonly burned) with a heat nearly sufficient to vitrify them, then reduced to powder by any mechanical or other operation, and the powder obtained is the basis of the cement.*

Roman cement was too quick-setting for use in foundations (Newby, 2001), but slowly gained popularity for use in work in contact with water (Blezard, 1998). Among those to appreciate Parker's Roman cement were Thomas Telford and Marc Isambard Brunel. Telford used Roman cement in the construction of the Chirck Viaduct (1796-1801), which carries Ellesmere Canal across the River Ceirog; backing the ashlar masonry sides with hard-baked bricks laid in Parker's cement to make it watertight (Davey, 1961; Hudson, 1972). Brunel used Parker's cement for the construction of the Wapping-Rotherhithe tunnel (Hudson, 1972) – the first tunnel under the River Thames (Davey, 1961). In fact, Roman cement was so popular that when his patent lapsed in 1810, it was feared that supplies of septaria on the Thames Estuary would become exhausted (Stanley, 1979); with over a million tonnes removed from the Harwick foreshore between 1812 and

1825 (Hudson, 1972). This lead to the Government prohibiting any digging closer than 50ft from the base of the cliffs, after which as many as 500 boats, each with a crew of three or four, were employed to dredge the septaria from the sea-bed (Hudson, 1972).

Following the success of Parker's Roman cement, there were notable attempts to produce higher quality cement by both L.J. Vicat and James Frost. Vicat carried out investigations on hydraulic lime, eventually preparing an artificial hydraulic lime by calcining a mixture of limestone (chalk) and clay, ground together in a wet mill (Blezard, 1998). In 1811 James Frost patented very similar hydraulic cement but, as the calcination temperature was too low, it was viewed to be inferior to Parker's Roman cement (Davey, 1961). A further patent (British Patent No. 4679) was taken out by Frost in 1822 for his 'British cement' – hydraulic cement in which the calcining temperature was high enough to drive off all the carbon dioxide in the mixture (Davey, 1961). In 1825 Frost established the first calcareous cement works in the London district when he opened his manufacturing plant at Swanscombe, Kent (Blezard, 1998). His British cement gained a better reputation in Britain and America than his previous product (Davey, 1961), but sold at a lower price than Roman cement (Blezard, 1998).

2.1.3.3 Portland cement

During this time Joseph Aspdin, a bricklayer from Leeds, was also working on his own cement. Aspdin had allegedly purchased a copy of Smeaton's *'A Narrative of the Eddystone Lighthouse'* in 1813 and probably tried to develop cement as a result of this (Stanley, 1979). It is possible that Aspdin's cement was created accidentally when he used a glass furnace instead of a lime kiln, burning the raw materials at a higher temperature than was practised (Hudson, 1972). Regardless, Aspdin received the patent (British Patent No. 5022) for his 'Portland cement' on 21 October 1824 (Stanley, 1979), in which he described his invention (Davey, 1961; Hudson, 1972):

> *I take a specific quantity of limestone such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle of powder, or the limestone, as the case may be to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labour or machinery. After this proceeding, I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by*

> *submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan until the water is entirely evaporated. Then I break the said mixture into suitable lumps and calcine them in a furnace similar to the lime kiln till the carbolic acid is entirely expelled. The mixture so calcined is to be ground, beat or rolled to a fine powder.*

Although Aspdin's early cement was still only a hydraulic lime, with a mineralogy and hydraulic activity very different from the product used today, his patent did give him the right to the term 'Portland cement' (Blezard, 1998), named so due to its resemblance to Portland stone in colour (Stanley, 1979) – a material which had a high reputation for quality (Hudson, 1972). It is possible that Joseph Aspdin's intention was actually for his cement to be used as an external grade plaster to render brickwork, producing a relatively cheap and aesthetic alternative to blocks of Portland stone, and did not fully appreciate the many potential uses it had (Stanley, 1979). Sometime between 1826 and 1828 Aspdin went into partnership with William Beverley, and the pair established their first cement works in Kirkgate, Wakefield (Stanley, 1979), soon after which, the superior Portland cement became a key construction material used for mass concrete works such as large-scale ports, docks and marine constructions (Idorn, 1997). Portland cement was put to one of its first major civil engineering uses after the collapse of Brunel's Thames Tunnel in 1828 (Stanley, 1979). Despite the fact that it was double the price of Roman cement, and in spite of strong opposition (Blezard, 1998), Brunel chose to use large amounts of Portland cement from the Wakefield works to effectively seal the breach until work recommenced in 1835 (Davey, 1961), when he was able to pump the tunnel dry and rebuild and re-line it with further Portland cement (Stanley, 1979).

Joseph Aspdin's younger son, William, spent nearly twelve years gaining experience and a thorough knowledge of his father's business before unexpectedly leaving the firm in July 1841 (Blezard, 1998), travelling 200 miles south to London where he set up a cement works at Rotherhithe, on the south bank of the River Thames, in the summer of 1843 (Stanley, 1979; Blezard, 1998). William Aspdin managed to manufacture an improved cement after he discovered that clinkered or 'over-burnt' material substantially increased the strength of the cement – though it is thought that his discovery was purely accidental due to his limited knowledge of chemistry (Blezard, 1998). This cement was found to be 2.4 times stronger than the best Roman cement and 20% stronger than the Portland-type cement produced by the company J.B. White (Blezard, 1998), with thin section micrographs revealing that his Portland cement exhibited the same clinker components

as we have in modern standard Portland cement (Idorn, 1997). Despite attaining vitrification in his kiln (Blezard, 1998), W. Aspdin did not understand the minerals or the reaction and was unable to reproduce the same product in every batch (Idorn, 1997).

It was I.C. Johnson (of J.B. White), who claimed to be the first to fully appreciate the importance of vitrification in the burning of raw materials (Davey, 1961; Blezard, 1998), that produced the first reliable Portland cement at Swanscombe, in Kent (Hudson, 1972; Davey, 1961). Johnson's discovery occurred when his kiln produced a material which was highly calcined and was in a state of semi-vitrification, and, upon pulverising, could be turned into a paste which turned very hard and had the colour of Portland stone. However, the set material fell apart when immersed in water and Johnson concluded it to be a failure, hiding it away, out of sight, in an isolated cellar where, several weeks later, he rediscovered the sample and found that the free lime had become slaked in the damp cellar. Upon retrying the sample, he found it turned perfectly hard and proved to be hydraulic (Davis, 1924).

He subsequently opened a second works, taking over William Aspdin's abandoned works at Gateshead (Blezard, 1998) in 1856, close to available sources of limestone and clay (Hudson 1972). His Portland cement, which was Portland cement as we now know it, only slowly replaced Roman cement in mortars and renders as it was much more expensive due to its high manufacture cost, and with few exceptions, it was not mixed with aggregates to make concrete for buildings until about 1865 (Hurst, 2001). Despite this, the cement industry soon became firmly established within the Thames Basin, with a significant concentration of works in North Kent where supplies of chalk, London clay and the mud deposits of the Thames and Medway were available, and transportation links along the Thames already established for the import of coal to the cement plants and the export of cement to London (Hudson, 1972).

2.2 PORTLAND CEMENT CHEMISTRY

While the term 'Portland cement' was patented in 1824, the composition and manufacturing process of that material was significantly different to that which we know today. Changes occurred over many years and were a result of the experimentation of both individuals and manufacturing companies, and also the introduction of national legislation – such as the British Standard Specification for Portland cement. An explanation of the cement chemist's notation used in the subsequent discussion can be found in Table 2-3. It should be noted, though, that, in cement chemistry, chemical formulae are often expressed as sums of oxides, but this does not imply that the constituent oxides exist separately within the structure (Taylor, 1997).

Table 2-3 – Cement Chemists' Notation

NOTATION	FORMULA	NAME
A	Al_2O_3	Aluminium oxide, alumina
C	CaO	Calcium oxide, lime
$\bar{C}$	CO_2	Carbon dioxide
F	Fe_2O_3	Iron (III) oxide, ferric oxide
K	K_2O	Potassium oxide
H	H_2O	Water
M	MgO	Magnesium oxide, magnesia
N	Na_2O	Sodium oxide
S	SiO_2	Silicon dioxide, silica
$\bar{S}$	SO_3	Sulfur trioxide, sulfuric anhydride
P	P_2O_5	Phosphorus pentoxide
T	TiO_2	Titanium dioxide
	CLINKER AND CEMENT CONSTITUENTS	
C_3S	$3CaO{\cdot}SiO_2$	Tricalcium silicate
C_2S	$2CaO{\cdot}SiO_2$	Dicalcium silicate
C_3A	$3CaO{\cdot}Al_2O_3$	Tricalcium aluminate
C_4AF	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	Tetracalcium aluminoferrite
$C\bar{S}$	$CaO{\cdot}SO_3$	Anhydrite
$C\bar{S}H$	$CaO{\cdot}SO_3{\cdot}2H_2O$	Gypsum
$C\bar{S}H_{0.5}$	$CaO{\cdot}SO_3{\cdot}\ 1/2H_2O$	Hemihydrate, bassanite
$C\bar{C}$	$CaO{\cdot}CO_2$	Calcium Carbonate
	CEMENT HYDRATION PRODUCTS	
CH	$CaO{\cdot}H_2O$	Calcium hydroxide, portlandite
C-S-H	$xCaO{\cdot}ySiO_2{\cdot}zH_2O$	Calcium silicate hydrate
$C_6A\bar{S}_3H_{32}$	$6CaO{\cdot}Al_2O_3{\cdot}3SO_3{\cdot}32H_2O$	Ettringite, trisulfoaluminate hydrate,
$C_4A\bar{S}H_{12}$	$4CaO{\cdot}Al_2O_3{\cdot}SO_3{\cdot}12H_2O$	Monosulfoaluminate hydrate, monosulfate,

Source: Adapted from Portland Cement Association (2004)

2.2.1 Hydration of Portland Cement

In order to comprehend the importance and implications of the changes that have occurred in Portland cement chemistry, it is first necessary to understand the hydration reaction which causes it to set, and the difference between hydration, setting and hardening. Odler (1998) defines cement hydration as *"the reaction of a non-hydrated cement or one of its constituents with water, associated with both chemical and physico-mechanical changes in the system, in particular with setting and hardening."* Additionally, the terms 'setting' and 'hardening' can be defined as the 'development of rigidity' and the 'steady increase in compressive strength', respectively (Bye, 1999).

Unlike traditional lime mortars which set and harden as a result of the reaction with atmospheric carbon dioxide (British Standards Institution, 2015b), Portland cement sets and hardens as a result of the hydration reaction which occurs when water is added – although, over time, carbonation of the hardened cement paste does result in a relatively small increase in surface strength (Neville, 2011).

2.2.1.1 Major Constituents

BS EN 197-1, the current standard for 'Cement', defines the major constituents of Portland cement as *"Specifically selected inorganic material in a proportion exceeding 5% by mass related to the sum of all the main and minor additional constituents* (British Standards Institution, 2011)"

While BS EN 197-1 and the criteria for modern Portland cement in the United Kingdom will be discussed in more detail in subsequent chapters, it useful to have a rough idea of cement composition during the present review of the hydration process. As such, clinker usually has a composition of approximately 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% other constituents (Taylor, 1997); normally as the four main phases with the following typical % of composition by mass of clinker:

Table 2-4 – Major constituents of Portland cement

CONSTITUENT	PHASE	TYPICAL %
Tricalcium silicate	Alite	50-70
Dicalcium silicate	Belite	15-30
Tricalcium aluminate	Aluminate	5-10
Tetracalcium alumina ferrite	Ferrite	5-15

Source: Data from Taylor (1997)

Calcium Silicates

The Portland cement constituents that are primarily responsible for strength gain are tricalcium silicate (C_3S) and dicalcium silicate (C_2S,) (Bye, 1999), in the impure, variable phases of alite and belite respectively, the hydration of which both produce calcium hydroxide (CH) and calcium silicate hydrate (C-S-H). However, alite is considered to be the most important constituent of Portland cement as it contributes most to the early strength gain and setting of the paste (Odler, 1998; Noor-ul-Amin, *et al*., 2013) – with 70% of alite reacting in the first 28 days, and almost all within the one year (Taylor, 1997).

That said, belite contributes little to strength in the first 28 days because it hydrates and gains strength much slower, and therefore contributes significantly more towards long-term strength development than early strength (The Concrete Society, 1987; Noor-ul-Amin, *et al*., 2013). However, under comparable conditions, the one-year strengths obtained from pure alite and pure belite are approximately the same (Taylor, 1997).

While the hydration of the calcium silicates is complex and not fully understood (Odler, 1998), if the assumption is made that the final product of hydration is $C_3S_2H_3$, then the *approximate* hydration reactions of alite and belite, and the corresponding masses involved, can be written as (Neville, 2011):

Tricalcium silicate hydration:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (1)$$

$$100 + 24 \rightarrow 75 + 49 \quad (2)$$

Dicalcium silicate hydration:

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad (3)$$

$$100 + 21 \rightarrow 99 + 22 \quad (4)$$

Therefore, for silicates of the same mass, although a similar mass of water is required for their hydration, C_3S produces more than double the amount of CH than the hydration of C_2S (Neville, 2011). However, in reality, the composition of calcium silicate hydrate is variable, and therefore usually referred to as 'C-S-H' – with the hyphens representing the indefinite composition (Bye, 1999) – as the term, 'CSH', would denote a specific composition of $CaO.SiO_2.H_2O$ (Taylor, 1997). Therefore, equations involving C-S-H are

often written in a non-stoichiometric form – meaning they are unbalanced approximations. As such, the hydration of C_3S can be written more generally as (Bye, 1999):

$$C_3S + (y + z)H \rightarrow C_xSH_y + zCH \quad (5)$$

Aluminate

The other two main constituents of Portland cement are tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF), however, the amount of these present in Portland cement is significantly less than the calcium silicates.

The presence of aluminate is, in some respects, problematic. Pure C_3A reacts vigorously with water, causing immediate 'flash set' (Bye, 1999; Neville, 2011), and so gypsum has to be added to cement clinker to act as a retarder to the formation of calcium aluminate hydrate; delaying it long enough to allow the setting of the cement paste to occur from the hydration of C_3S (Neville, 2011). Furthermore, C_3A makes little contribution to strength development (The Concrete Society, 1987; Bye, 1999) and is susceptible to sulfate attack – which can result in detrimental expansion within the hardened paste when calcium sulfoaluminate is formed (Neville, 2011). However, C_3A does have two properties which are of merit in cement production: firstly, it acts as a flux – reducing the temperature of clinker burning, and, secondly, it facilitates the combination of lime and silica (Neville, 2011).

The hydration of C_3A produces the hexagonal crystals of calcium aluminate hydrate C_2AH_8 and C_4AH_{19}, but this eventually converts to cubic C_3AH_6, known as 'hydrogarnet' (Odler, 1998; Mindness & Young, 1981):

$$C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \quad (6)$$

$$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H \quad (7)$$

Therefore, the final reaction can be summarised as (Neville, 2011):

$$C_3A + 6H \rightarrow C_3AH_6 \quad (8)$$

However, in the presence of calcium sulfate (gypsum), the product of C_3A hydration is a sulfoaluminate, the AFt phase known as 'ettringite' with the chemical formula $C_6A\bar{S}_3H_{32}$ (Bye, 1999; Odler, 1998):

$$C_3A + 3C\bar{S}H + 26H \rightarrow C_6A\bar{S}_3H_{32} \quad (9)$$

Once the supply of calcium sulfate is depleted, the initial ettringite formed will then react with any excess C_3A, resulting in the formation of calcium aluminate monosulfate hydrate, the AFm phase known as 'monosulfate', as shown below (Bye, 1999; Odler, 1998):

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12} \quad (10)$$

However, as the ettringite supply is depleted, C_4AH_{19} will begin to form, either in solid solution with $C_4A\bar{S}H_{12}$, or as the separate crystals previously mentioned (Odler, 1998).

Ferrite

Tetracalcium aluminoferrite (C_4AF) is formed as a result of the use of iron and aluminium raw materials to reduce the clinkering temperature during cement manufacture (Kosmatka, *et al*., 2002). Under comparable conditions, the hydration products formed by ferrite are usually described as being similar to those formed by aluminate (Odler, 1998; Bye, 1999; Taylor, 1997), with AFt phases formed when calcium sulfate is present, and AFm phases formed in its absence (Taylor, 1997). However, unlike C_3A, C_4AF never hydrates rapidly enough to cause flash set, and the retardation caused by the addition of calcium sulfate is more significant for C_4AF than C_3A (Mindness & Young, 1981).

The hydration reactions of ferrite are shown below, with the term *'(A,F)'* indicating that iron oxide and alumina occur interchangeably in the compound without the need for the A/F ratio to be the same as the parent compound (Mindness & Young, 1981):

$$C_4AF + 3C\bar{S}H_2 + 21H \rightarrow C_6(A,F)\bar{S}_3H_{32} + (A,F)H_3 \quad (11)$$

$$C_4AF + C_6(A,F)\bar{S}_3H_{32} + 7H \rightarrow 3C_4(A,F)\bar{S}H_{12} + (A,F)H_3 \quad (12)$$

2.2.1.2 Hydration Products

The hydration products can be defined as two groups: sometimes referred to as 'inner' and 'outer' products. The inner products form within the boundaries of the original anhydrous grains, while the outer product fills the space that was originally filled with water. Calcium hydroxide is mainly an outer product, and although C-S-H forms as both an inner and outer product, the structures of these are different – the Ca/Si ratio being higher in the outer product (Odler, 1998).

While the composition of a hardened cement paste varies as a result of multiple factors, Taylor (1997) was able to calculate the following composition – including pores and residual cement particles, of a typical 14-month-old, saturated Portland cement paste with 0.5 w/c (water/cement ratio):

Table 2-5 – Calculated volume percentages based on phase composition and densities

Alite	Belite	Aluminate	Ferrite	Insol. Res.	C-S-H	CH	AFm	AFt	Hydro-garnet	Hydro-talcite	Pores
1.0	0.6	0.0	1.0	0.1	48.7	13.9	11.1	3.6	2.2	1.8	16.0

Source: Adapted from Tayler (1997)

However, when considering the hydration products only, compositions are usually in the typical ranges found in Table 2-6:

Table 2-6 – Typical volume percentages of hydration products

CONSTITUENT	PHASES	TYPICAL %
Calcium silicate hydrate	C-S-H	50-60
Calcium hydroxide	CH	20-25
Calcium aluminate hydrates	AFt, AFm	15-20

Source: Original data from Mehta & Monteiro (2006)

Calcium Silicate Hydrate

As previously mentioned, C-S-H has an indefinite composition, but is sometimes approximated to $C_3S_2H_3$ as the C/S ratio usually varies between 1.5 and 2.0 (Mindness & Young, 1981). However, this ratio has been found by some researchers to vary from as much as 1.2 to 2.3, with a mean of approximately 1.75, in neat Portland cement pastes (Richardson, 1999). This variation can be attributed to several factors such as the age of the paste, the hydration temperature, the w/c ratio and the oxide impurities that may be present (Mindness & Young, 1981).

Since C-S-H is the main product of Portland cement hydration it has a significant effect on the properties of hardened cement paste. C-S-H is made up of a collection of very small, almost amorphous particles (Bye, 1999) with varying morphology, and, as a result of its variability and low degree of crystallinity, it is a difficult material to study (Mindness & Young, 1981). However, it is generally agreed that C-S-H has a structure of layered calcium silicate sheets and interlayer space where micropores are formed. These micropores, or 'gel pores', that exist in C-S-H are different from capillary pores; which are larger voids – originally filled with water or air (Bye, 1999), in which water behaves as bulk water and menisci can form as they are filled or emptied (Mindness & Young, 1981).

In regards to historic literature, it is worth noting that C-S-H has previously been referred to as 'tobermorite gel' as it was thought to resemble the natural mineral tobermorite – chemical formula $Ca_5Si_6O_{16}(OH)4H_2O$ (Mehta & Monteiro, 2006) – and although this terminology has since been abandoned due to its inaccuracy, the term 'C-S-H gel' is sometimes used to distinguish the material formed in cement pastes from other varieties of C-S-H (Taylor, 1997).

Calcium Hydroxide

Unlike C-S-H, calcium hydroxide has a definite stoichiometry, and is coarsely crystalline as hexagonal prisms – sometimes forming crystals in concrete voids that are large enough to be seen with the naked eye. While they do not grow that large within the body of the paste, they are still large enough to be seen under an optical microscope (Mindness & Young, 1981). However, when compared to C-S-H, calcium hydroxide offers little potential strength-contribution and has a considerably lower surface area (Mehta & Monteiro, 2006).

Calcium Sulfoaluminates

The amount of the AFt (trisulfate) and AFm (monosulfate) phases formed is not only dependent on the amounts of aluminate and ferrite phases present in the original cement, but also the degree of hydration as, after reaching a maximum, the amount of AFt present decreases and the amount of AFm increases to the point that AFt may be completely depleted in a mature paste (Odler, 1998).

Ettringite, the most important AFt phase, forms during the early hydration of most Portland cement (Taylor, 1997) and, like calcium hydroxide, ettringite crystals also form as hexagonal prisms. However, ettringite crystals have a much greater aspect ratio, and so have the distinct appearance of long slender needles (Mindness & Young, 1981). As previously mentioned, ettringite will eventually transform to the AFm phase monosulfate hydrate, $C_4A\bar{S}H_{12}$, which forms as hexagonal-plate crystals, and is notably susceptible to sulfate attack (Mehta & Monteiro, 2006).

With regards to the analysis of hardened cement, it is also important to mention that ettringite loses a considerable amount of its water on drying (Mindness & Young, 1981), with water loss commencing rapidly at about 50°C in ordinary humidity (Taylor, 1997).

2.2.1.3 The Effect of Hydration on Cement Paste Structure

C-S-H and the calcium aluminate phases have enormous surface area and adhesive capability, and so strongly adhere to one another and also to any low surface area solids, such as calcium hydroxide, anhydrous clinker grains, and fine and coarse aggregate particles (Mehta & Monteiro, 2006). Therefore, as the volume of hydration products increases, the number of contacts between particles also increases, resulting in the formation of a continuous network of solids within the paste (Odler, 1998).

Furthermore, since the hydration products have a volume more than double that of the original cement phases, as hydration progresses and the volume of hydration products increases, the volume of capillary pores is reduced – but the total volume of gel pores increases (Neville, 2011). While, in mature cement pastes, the bulk of the porosity is within the C-S-H (Mindness & Young, 1981), these micropores have a nominal diameter of less than 2-3nm, which is one or two orders of magnitude less than that of capillary pores, and only one order of magnitude greater than the size of water molecules (Neville, 2011).

Consequently, while it is logical to assume that voids are detrimental to the hardened paste, the gel pores are too small to directly have an adverse effect on the strength and permeability of the hardened cement paste, but water removal from them may contribute to durability issues such as drying shrinkage and creep (Mehta & Monteiro, 2006). A more detailed classification of the pores in hardened cement pastes can be found in Table 2-7:

Table 2-7 – Classification of pores in hardened cement pastes

DESIGNATION	DIAMETER	DESCRIPTION	ROLE OF WATER	PROPERTIES INFLUENCED
Capillary Pores	10-0.05 μm	Large capillaries	Bulk water	Strength, permeability
	50-10 nm	Medium capillaries	Menisci generate moderate surface tension forces	Strength, permeability, shrinkage at high humidity
Gel pores	10-2.5 nm	Small (gel) capillaries	Menisci generate strong surface tension forces	Shrinkage to 50% RH
	2.5-0.5 nm	Micropores	Strongly adsorbed water, no menisci	Shrinkage, creep
	< 0.5 nm	Micropores	Structural water involved in bonding	Shrinkage, creep

Source: Reproduced from Bye (1999)

2.2.2 Cement Manufacturing Process

Modern Portland cement clinker is produced by burning a mix of calcium carbonate and aluminosilicate and then ground with approximately 5% gypsum to produce Portland cement (Bye, 1999). As previously discussed, the calcium silicate phases, alite and belite, are essential to the strength gain of Portland cement, and both of these phases form above 800°C – with alite preferentially formed at higher temperatures and calcium oxide contents (Noor-ul-Amin, *et al*., 2013).

While some of the historic sources of raw materials used in Portland cement manufacture have been previously discussed, a more comprehensive list of sources which have been used, including industrial by-products, can be found in Table 2-8 – where the * denotes those most commonly used:

Table 2-8 – Sources of raw materials used in manufacture of Portland cement

CALCIUM	IRON	SILICA	ALUMINA	SULFATE
Alkali waste	Blast-furnace flue dust	Calcium silicates	Aluminium-ore refuse*	Anhydrite
Aragonite*	Clay*	Cement rock	Bauxite	Calcium sulfate
Calcite*	Iron ore*	Clay*	Cement rock	Gypsum*
Cement-kiln dust	Mill scale*	Fly ash	Clay*	
Cement rock	Ore washings	Fuller's earth	Copper slag	
Chalk	Pyrite cinders	Limestone	Fly ash*	
Clay	Shale	Loess	Fuller's earth	
Fuller's earth		Marl*	Granodiorite	
Limestone*		Ore washings	Limestone	
Marble		Quartzite	Loess	
Marl*		Rice-hull ash	Ore washings	
Seashells		Sand*	Shale*	
Shale*		Sandstone	Slag	
Slag		Shale*	Staurolite	
		Slag		
		Traprock		

Source: Adapted from Kosmatka, *et al*. (2002)

Once the raw materials arrive at the cement works, they are crushed, milled, and proportioned to achieve the desired chemical composition. This process can be carried out wet or dry and, in most respects, the two processes are very similar – the main difference being that, in the wet process, the milling and blending are carried out with the materials in a slurry form. Once this process is complete, the raw mixture is passed through a kiln, where it is chemically altered at temperatures between 1400-1550°C – turning it into cement clinker, with the appearance of marble-sized greyish-black pellets. This is then cooled, combined with approximately 5% gypsum and ground until the

powder, which is now technically Portland cement, passes through a 45μm sieve (Kosmatka, *et al*., 2002).

2.2.2.1 Locations of Cement Works

Historically it was common for cement works to be established in close proximity to supplies of suitable quality raw materials, such as the chalk, marl and clay on the Thames, Medway and the South coast of England, the chalklands North East of London, and the chalk ballast from coal transport ships returning to the North East coast of England (Jackson, 1999).

However, the lack of available raw materials placed limits on the growth of the Scottish cement industry. In total, only four cement works operated in Scotland between 1906 and 1959 – all of which are now closed. To this day, only one other cement works has opened in Scotland; the Dunbar works which opened in 1963 and is still in use.

The first cement works in Scotland opened at Cousland, 13km South East of Edinburgh, in 1906, and used carboniferous limestone and shale to produce 300 t/week from four Schneider kilns. By 1912 the Glasgow Iron and Steel Company had established an activated slag works at Wishaw, 22km south-east of Glasgow, which eventually began to produce Portland cement from carboniferous limestone delivered by rail from the Cousland area and Harburn in West Lothian, as well as ground blastfurnace Portland cement – using slag from their Wishaw Iron Works. A similar works was opened at Newmains by the Coltness Iron Company, who initially processed slag from their Coltness iron works, but in 1914 began to produce Portland cement and ground blastfurnace Portland cement in two Pfeiffer rotary kilns (Jackson, 1999; Moore, 2011).

Table 2-9 – Cement works established in Scotland

LOCATION	East Lothian	Lanarkshire			Midlothian
	Dunbar	**Newmains**	**Gartsherrie**	**Wishaw**	**Cousland**
Clinker Manufacture Operational	1963 to date	1914 to 1959	1918 to 1958	1920 to 1958	1906 to 1923
Raw Materials	Carboniferous Limestone from 1963-1982: South Quarry, 1982-2006: Northwest Quarry, 2006 to date: Northeast Quarry.	Carboniferous Limestone from Oxwell Mains, Dunbar, East Lothian, supplemented by stone from Llangoed, Anglesey. Blastfurnace slag: 1914-1927 from the Coltness Ironworks: after 1927, bought in from surrounding plants. Sandstone.	Carboniferous Limestone from the Cousland area. Blastfurnace slag from Baird's Gartsherrie Ironworks.	Carboniferous Limestone from the Cousland area and from Harburn, West Lothian. Blastfurnace slag from the Wishaw Iron Works until 1930, and subsequently from other plants around the Motherwell area.	Carboniferous Limestone from quarry. There seems to have been a drift mine as well. Colliery waste; there were six collieries within 3 km.
Ownership	1963-2001: Blue Circle 2001-2013: Lafarge 2013- : Lafarge Tarmac	Coltness Iron Co. Ltd	1918-1938: William Baird & Co. Ltd 1938-1946: Baird's & Scottish Steel Ltd 1967-1986: Clyde Portland Cement Co. Ltd (Tunnel) 1986-2006: Castle Cement Ltd (RTZ to 1989, Scancem to 1999, Heidelberg Cement to 2006)	1912-1967: Glasgow Iron and Steel Co. 1967-1970: GI&SC/APCM joint venture. 1970-1974: APCM.	1906-1911: Caledonian Cement Co. Ltd 1911-1924: BPCM (Blue Circle)

Source: Original data from Moore (2011) and Jackson (1999)

2.2.3 Historic Portland Cement Composition

There are limited data on the composition of early Portland cement in the United Kingdom. However, an analysis of Joseph Aspdin's cement was conducted in 1849 by Professor Pettenkofer. Although it is not possible to determine the actual degree of calcination of Aspdin's cement, Pettenkofer's analysis, shown in Table 2-10, reveals that the cement had a relatively high alkali content and contained P_2O_5 – suggesting that the firing temperature was not very high (Gooding & Halstead, 1952).

Table 2-10 – Analysis of Joseph Aspdin's Portland cement and typical modern CEM I

COMPOUND	ASPDIN'S CEMENT %	TYPICAL MODERN CEM I %
Alkalis	2.8	-
Alumina, Al_2O_3	7.8	5.4
Carbon dioxide, CO_2	2.2	-
Chemically combined water	1.0	-
Insoluble residue	2.2	-
Iron oxide, Fe_2O_3	5.3	2.6
Lime, CaO	54.1	64.5
Magnesia, MgO	0.8	1.6
Phosphoric anhydride, P_2O_5	0.8	-
Silica, SiO_2	22.2	20.2
Sulfuric anhydride, SO_3	1.0	2.8
Total	*100*	*97.1**

Source: Adapted from Gooding & Halstead (1952), original data from Becker (1869)
* Shortfall for minor additional constituents

Another early Portland cement analysis was carried out on the orders of I.C. Johnson as he tried to determine the secrets of Aspin's cement. He obtained a sample of the cement and had it analysed by a chemist in London (Davis, 1924). The analysis, found in Table 2-11, shows the presence of a considerable proportion of calcium phosphate – a compound which Johnson knew was not found in the Thames chalk and Medway clay which Aspdin used as raw materials. It was thought that Aspdin had used bone ash as a flux in his raw material (Gooding & Halstead, 1952) and Johnson consequently procured old bones which were calcined, pulverised and added to his own raw mixture – an experiment which resulted in failure (Davis, 1924).

Table 2-11 – Analysis of William Aspdin's Portland cement

COMPOUND	%
$Ca_3(PO_4)_2$	45.00
CaO	22.24
$CaCO_3$	10.00
$CaSO_4$	15.00
FeO	3.26
Al_2O_3	1.00
H_2O	1.00
Soluble saline matter	2.50
H_2SO_4	Trace
Total	*100.00*

Source: Davis (1924)

2.2.4 Introduction of Cement Standards

The start of the 20th century saw two particular events which had a significant effect on how Portland cement would be manufactured in the United Kingdom in the future. The first of these was the amalgamation of 27 cement manufacturers to form The Associated Portland Cement Manufacturers (1900) Ltd, also known as the APCM, which was established with the hope that it would have the advantage of pooling experience and allow the sharing of each company's economic discoveries, while eliminating the unnecessary competition – both in raw material purchase and disposal of the finished product (Cook, 1958). As a result, by 1907 the state of the cement industry was very different, with improvements in mixing, grinding and the overall efficiency of production.

The second event was the introduction of what would become BS 12 – the British Standard Specification for Portland cement, first issued by the Engineering Standards Committee of the ICE in 1904 (The Engineering Standards Committee, 1904; Somerville, 2001). This first standard for Portland cement clearly outlined requirements for the quality, preparation, testing and acceptance of Portland cement – successfully providing, for the first time, a nationwide standard to which the British cement industry had to adhere. Prior to this each user had to provide their own specification, so the introduction of a standard for Portland cement was beneficial to both its users and manufacturers – to the users as they no longer had the trouble of providing a specification of their own, and to the manufacturers as they no longer had to meet the varying specifications they received from numerous clients (Butler, 1923). Since then there have been 15 editions of BS 12, throughout which there have been successive changes to the limits and

requirements set, as well as the methods of testing and sampling, which have arisen as a result of the improvements in manufacturing technology and technical knowledge.

When presenting a paper on the British Standard Specification for Portland cement at the Institution of Structural Engineers in June 1923, D.B. Butler expressed his concern that the current edition of British standard needed to be revised as testing requirements were too lax and must be improved if British cement was to remain competitive in the global market (Butler, 1923). In his paper, Butler compared the British standard to the standards of other nations and concluded that of particular concern were Britain's requirements for fineness and strength testing – this was in spite of four revisions of the standard that had been published in 1907, 1910, 1915 and 1920, which had already the introduction of stricter requirements.

With regards to fineness of grinding, the original 1904 edition of BS 12 (The Engineering Standards Committee, 1904) stated that:

> *The residue on a sieve 76 x 76 = 5776 meshes per square inch, shall not exceed 3 percent.*
>
> *The residue on a sieve 180 x 180 = 32,400 meshes per square inch, shall not exceed 22.5 percent.*

The limit of residue on an 180 x180 was subsequently lowered to 18% in 1907 and further lowered to 14% in 1915 (Butler, 1923) where it still stood in 1923 when Butler addressed the Institution. Butler felt this was still "far too high" in view of cement mill practice at that time, especially given the fact that for export purposes it was ground to 5% in order to account for global competition, and instead recommended a limit of 8 or 10%, despite the extra cost that this would inevitably cause to the manufacturer.

The early editions of BS 12 did not give requirements for compressive strength testing, despite this being the normal practice at the time in Germany and more generally on the continent, and instead relied on tensile strength tests which were more convenient and less expensive to carry out (Butler, 1923). The 1904 edition fixed the minimum 7-day neat test at 400 psi, and the sand test at 150 psi, with a proportionate increase in each after 28 days. By the 1914 edition, the minimums were raised to 450 and 200 psi respectively, where they still stood at in 1923 (Butler, 1923). Butler, however, argued that these were too low and suggested that they should be raised to 600 psi neat and 300 psi for sand, because the best Portland cement manufactured at that time developed a tensile strength

of almost double these and, in his opinion, any samples reported to be lower were below the average of good Portland cement.

Further to these observations, Butler concluded that the British Standard Specification for Portland cement was considerably weaker than its American and Argentine government counterparts (Butler, 1923). This meant that the cement reaching the minimum conditions of the British standard was poorer than that meeting the minimum condition of its global competitors and that the British standard had to be improved in order to force the British cement to rival foreign competition.

Another feature of the specification for Portland cement was the limit on the ratio of CaO to SiO_2 and Al_2O_3, which could not exceed 2.75. This was revised in the 1915 edition to the ratio shown in Equation 13 which had to be within the range 2.0 to 2.85 – later further revised to between 2.0 and 3.0. This was included to ensure that users were offered a product containing hydraulically active calcium silicates (Corish & Jackson, 1982).

$$\frac{0.0179\ (\%CaO)}{0.0167\ (\%SiO_2) + 0.0098\ (\%Al_2O_3)} \tag{13}$$

However, Corish & Jackson (1982) state that the lower limits of this ratio rarely had to be used, as even Aspin's Portland cement from 1848 had a ratio of 2.48. Although cement manufacturers understood that higher values of this ratio granted higher strength, the limitations of cement manufacturing facilities at that time meant that to raise this value also increased the difficulty in combining and controlling the feedstock – ultimately leading to an unsound product (Corish & Jackson, 1982). With this in mind, manufacturers did not increase the ratio past 2.8 which, assuming a 3% uncombined lime content, limited the tricalcium silicate (C_3S) content to an effective maximum of 45% (Corish & Jackson, 1982).

Although the required test methods in the USA were different from those in Britain – making it impossible for direct comparison (Corish & Jackson, 1982) – the data from a detailed investigation of American cements by Gonnerman & Lerch (1952) suggests similar to trends to those found in Britain by Corish & Jackson (1982) and Corish (1994). Cement compositions published by Corish & Jackson (1982) are shown in Table 2-12.

In their 1952 paper, Gonnerman & Lerch reviewed a series of tests on Portland cement, carried out between 1904 and 1950, and discussed the changes in composition and

properties that occurred during this period. Among their conclusions was, unsurprisingly, that the earlier tests indicated much wider fluctuations in the cement compositions – in particular in the period 1904 to 1926. Although the average C_3S content of the cement during this period was significantly lower than the corresponding average in 1952, some of the 1904 cement did have potential contents just as high as those of 1952. Gonnerman & Lerch also concluded that the most significant changes in composition occurred between 1926 and 1933, with no significant changes occurring between 1933 and 1950. The main changes in composition between 1926 and 1933 consisted of "a gradual decrease in average SiO_2 and an increase in average CaO which resulted in an increase in the average computed C_3S content from about 33% to about 50%, and a decrease in computed C_2S content from about 40% to about 25%" (Gonnerman & Lerch, 1952).

Table 2-12 – Chemical properties of cement

COUNTRY OF ORIGIN	YEAR	% C_3S		% C_2S		% C_3A		BS12 : 1978 LSF		% FREE LIME USED IN CALCULATING % C_3S & C_2S
		TYPICAL	TYPICAL RANGE	TYPICAL	TYPICAL RANGE	TYPICAL	TYPICAL RANGE	TYPICAL	TYPICAL RANGE	
UK	1848	14	-	46	-	12	-	0.86	-	3.5
UK	1883	4	-	63	-	14	-	0.80	-	3.0
USA	1904	28	-	47	-	13	-	-	-	2.5
USA	1909-18	26	-	47	-	12	-	-	-	2.5
USA	1921-25	26	-	46	-	12	-	-	-	2.0
UK	1914-22	25	15-48	44	26-51	14	10-16	0.87	0.84-0.93	2.5
UK	1928-30	43	19-58	29	13-54	11	8-13	0.92	0.82-0.98	2.5
USA	1926-30	32	-	40	-	12	-	-	-	2.0
USA	1931-35	41	-	31	-	11	-	-	-	2.0
UK	1939	40	-	33	-	11	-	0.90	-	1.8
USA	1936-40	44	-	29	-	11	-	-	-	1.5

Source: Corish & Jackson (1982)

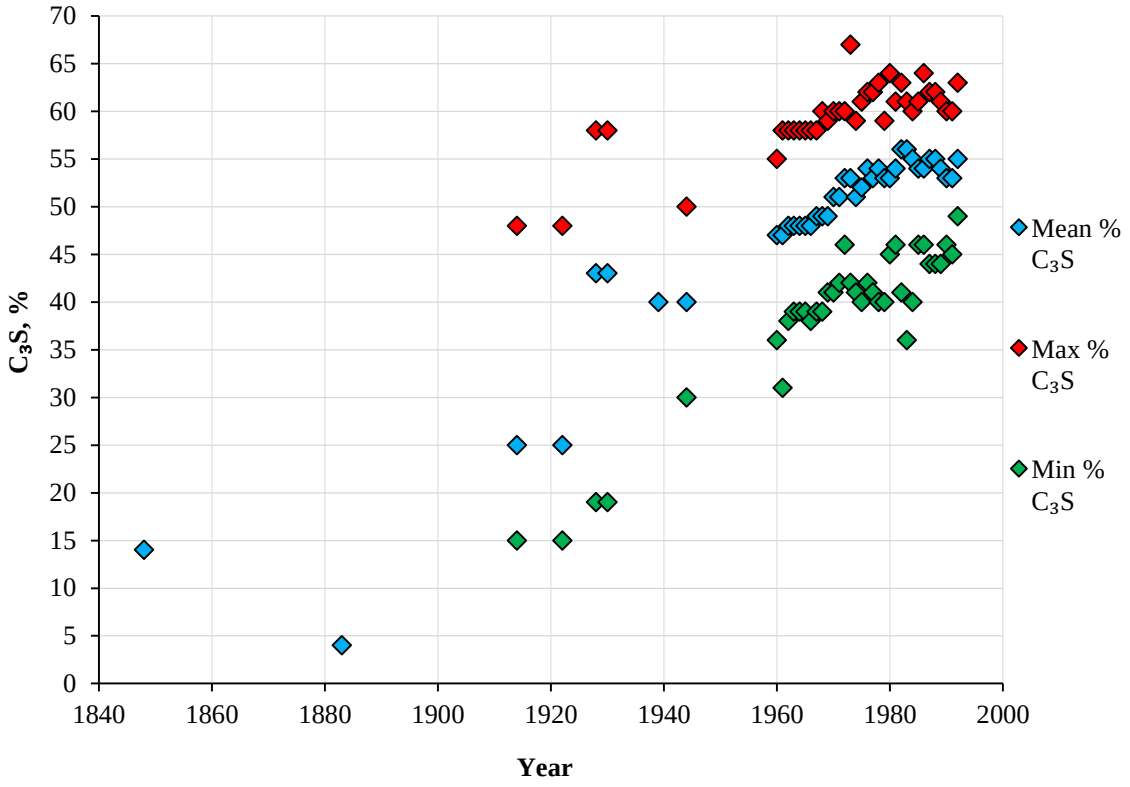

Figure 2-1 – Typical tricalcium silicate content, original data from Corish & Jackson (1982)

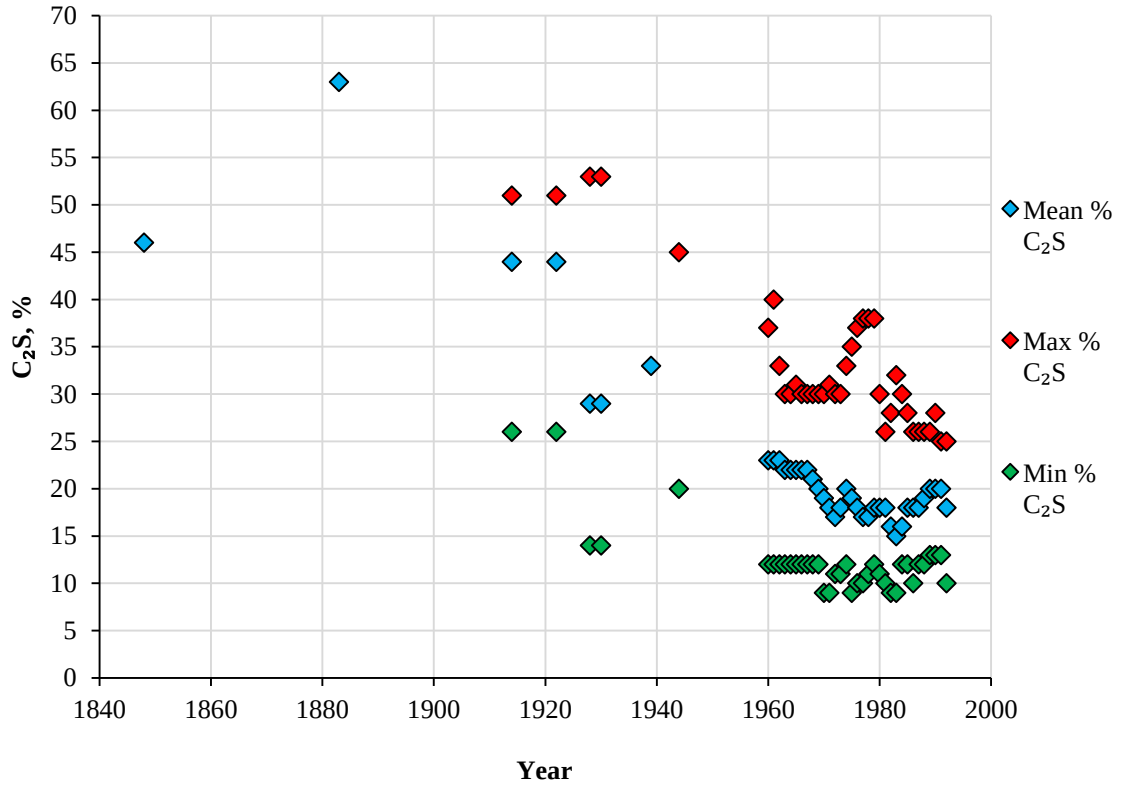

Figure 2-2 – Typical dicalcium silicate content, original data from Corish & Jackson (1982)

2.2.5 Modern Portland Cement Composition

The production, composition and testing of cement are now far more strictly governed by both national and international standards. In the United Kingdom, the requirements for cement are laid out in both British and European Standards. These standards not only cover the specification, conformity criteria and testing procedures for Portland cement, but also a range of blended and specialist cement types.

One such standard is BS EN 197-1 (British Standards Institution, 2011) - the British Standard for Cement, which defines 27 common cement products, in respect to five main cement types. These five cement types are:

- CEM I – Portland cement
- CEM II – Portland composite cement
- CEM III – Blastfurnace cement
- CEM IV – Composite cement
- CEM V – Composite cement

The composition requirements for each of these five cement types are outlined in BS EN 197-1, with CEM I composed of 95-100 percent by mass of clinker, with an allowance for 0-5 percent by mass for minor additional constituents, which may be added to improve the physical properties of the cement. The standard also gives the following definition and requirements for Portland cement clinker:

> *Portland cement clinker is made by sintering a precisely specified mixture of raw materials (raw meal, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. The raw meal, paste or slurry is finely divided, intimately mixed and therefore homogenous.*
>
> *Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ($3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$), the remainder consisting of aluminium and iron-containing clinker phases and other compounds. The ratio by mass $(CaO)/(SiO_2)$ shall be not less than 2,0. The content of magnesium oxide (MgO) shall not exceed 5,0 % by mass.*

Table 2-13 – Typical analyses of types of cement currently available in the UK

	PORTLAND CEM I	**LIMESTONE** CEM II/AL OR LL	**BLASTFURNACE** CEM III	**PORTLAND FLY ASH** CEM II/B-V
	%	*%*	*%*	*%*
CaO	64.5	62	51	51
SiO_2	20.2	16	16	26
MgO	1.6	1	7	2
Al_2O_3	5.4	3	9	11
Fe_2O_3	2.6	5	2	5
SO_3	2.8	2	2	3

Source: BS 1181-124: Appendix B (British Standards Institution, 2015a)

Given the changes in standard test procedures that have occurred since BS 12 was first introduced in 1904 and the lack of historic test data, it is difficult to draw direct comparisons between the physical properties of historic and modern cement.

One such change in test procedures was the move towards compressive strength testing over tensile strength testing. Modern Portland cement is supplied in three main strength classes (British Standards Institution, 2011): 32.5, 42.5 and 52.5 N/mm, where the strength indicates the 28-day compressive strength of mortar consisting of one part cement, three parts CEN standard sand, and one half part of water (w/c 0.5), with each mortar batch for three test specimens consisting of 450 ± 2g of cement, 1350 ± 5g of sand and 225 ± 1g of water (British Standards Institution, 2016).

However, there are some direct comparisons that can be made due to consistencies in the content of BS 12, such as the inclusion of insoluble residue limits. The original version of BS 12 enforced an insoluble limit of 1.5% and this was still the case in the final version of BS 12 (British Standards Institution, 1996a), provided the cement contained no additional minor constituents – in which case the limit was 5%, as it is now for CEM I (British Standards Institution, 2011).

2.3 THE DEVELOPMENT OF REINFORCED CONCRETE & PROPRIETARY SYSTEMS

Although improvements in cement chemistry in the 1800s led to a stronger material with a wider range of applications, the use of concrete in construction was hindered by the fundamental issue of its tensile capacity. While concrete is very strong in compression, it is relatively weak in tension, and so the structural use of concrete was confined to relatively large, mass concrete structures which carried the load in compression. Examples of the ingenuity to which the compressive strength of mass concrete was particularly well utilised in Scotland can be found in the viaducts on the West Highland Railway – the most spectacular, and famous, being the Glenfinnan Viaduct, constructed by Sir Robert 'Concrete Bob' McAlpine in 1897, which features twenty-one 15m spans (Addis & Bussell, 2003).

However, in the second half of the 19th Century, many attempts, with varying success, were made to increase the tensile capacity of concrete by adding iron, and later steel, reinforcement. The first mention of reinforced concrete in the 19th Century can be credited to an 1830 publication entitled, *'The Encyclopaedia of Cottage, Farm and Village Architecture,'* which suggested that a lattice of iron rods could be embedded in concrete to form a roof (Lambert, 2002). However, there is no evidence of its application, and it was many years before the first recorded uses of reinforced concrete.

As multiple different reinforcement systems were used throughout this period, it is likely that a variety of these systems could be encountered during the conservation of historic concrete structures in Scotland, and, therefore, knowledge of the various reinforcement systems that were employed is important.

2.3.1 Pioneers of Reinforced Concrete

2.3.1.1 William Wilkinson

It was at the Gateshead cement works that Newcastle upon Tyne plasterer William Boutland Wilkinson gained an understanding of the applications of Portland cement (Davey, 1961). Often credited with the invention of reinforced concrete (Stanley, 1979), Wilkinson was granted a patent on 27 October 1854 (Cassie, 1955) for *'Improvements in the construction of fireproof dwellings, warehouses, other buildings and parts of the same'*. The patent (British Patent No. 2293), which was the first to use reinforced concrete as a composite structure – embedding a network of flat iron bars or wire rope in

floors or beams of flat or arched concrete (British Cement Association, 1999) – showed that Wilkinson understood the relative weakness of concrete in tension (Bussell, 2001b).

Wilkinson's patent was never adopted by the building industry (Hurst, 2001) and there is little evidence remaining to show what extent he made use of it himself (Brown, 2001; Stanley, 1979). However, it was applied by Wilkinson in the construction of a cottage sometime around 1865 (Cassie, 1955), built at the site of his concrete works on a plot behind Ellison Place in Newcastle (Brown, 2001). The cottage was built entirely of reinforced concrete (Cassie, 1955) and remained in excellent condition until it was demolished in 1954.

It should be noted that, although there are several examples of iron-reinforced concrete prior to Wilkinson's, these merely feature metalwork encased in concrete (British Cement Association, 1999) rather than a composite reinforced concrete. Examples include the reinforced concrete plant pots made by French engineer Joseph Monier in 1849 (Stanley, 1979; de Courcy, 2001) and patented in 1867, the decorative Fluers-de-Lys at William Aspdin's Portland Hall, built in 1850 (Blezard, 1998) and the world's first reinforced concrete boat, constructed by French lawyer Jean-Louis Lambot in 1848 (Stanley, 1979) who created it by plastering a layer of fine concrete over a network of iron rods and mesh – producing what is now known as ferro-cement (British Cement Association, 1999).

2.3.1.2 François Coignet

Another significant developer in the history of reinforced concrete was Frenchman François Coignet. Coignet, who was primarily a chemical engineer (de Courcy, 2001), had spent several years studying concrete and began building in mass concrete cast *in-situ* in 1847. In 1852 or 1853 (Collins, 1959) he used concrete for the construction of his new chemical factory at St. Denis, outside Paris – the walls, vaulting, stairs and lintels of which were made entirely of concrete. He later built a four-storey house, opposite the factory, which featured exposed concrete replicating a typical stone building (Newby, 2001), upper floors fireproofed by encasing timber beams in lime concrete and a flat concrete roof which was strengthened with iron beams (Collins, 1959).

Coignet continued to experiment with concrete in France before filing for two French patents (*'Béton Economique'* and *'Emploi du Béton'*) on 29 March 1855 – one of which explained the possibilities of using cheap aggregates, and the other his methods for building monolithic concrete structures. Then on 26 November 1855 (Collins, 1959), the

year after Wilkinson was granted his patent, Coignet applied for the patent *'Artificial Stone and Cement'* (British Patent No. 2659) (de Courcy, 2001), in which he described his construction method for floors (Collins, 1959):

> *This new description of floorings is established by laying on the walls to support the flooring certain number of iron stop planks, parallel to one another, and reposing on the walls by their ends, so as to be completely supported by the whole thickness of the wall... but instead of iron planks I can establish iron rods placed at convenient distances apart from the other, and traversing through and through the four walls supporting the flooring, so that these iron rods cross symmetrically one another and look somewhat like a chessboard. These rods, being in the shape of a screw and having a nut at each end, will prevent the walls from losing their perpendicularity.*

Although Coignet's patent attracted little interest from the British building industry (Bussell, 2001b), he received recognition for his work in France, where he established himself as a serious building contractor in 1861 (Collins, 1959). That same year he also published *'Bétons aggolmérés'* – a book promoting the use of the material in which any binder could be used, as the importance was instead placed on the careful mixing and thorough compaction (de Courcy, 2001). Coignet continued to design and build using mass concrete, demonstrating it to be an effective material in projects such as the church at Le Vesinet, built in 1962 (Newby, 2001).

2.3.1.3 Joseph Tall & Charles Drake

Back in Britain, it was the English contractor Joseph Tall who was the first to develop the ideas of Coignet (Collins, 1959); constructing some of the earliest reinforced concrete buildings (British Cement Association, 1999). Realising that the majority of the cost associated with concreting works at the time was due to the timber formwork (Collins, 1959), he focused on developing a standardised, reusable shuttering system which he patented in 1865 (No. 822) (Newby, 2001). Tall demonstrated this system in a pair of concrete cottages which he built in Bexleyheath, Kent in 1866. The monolithic concrete walls of the cottages were cast *in-situ* using his patented formwork (British Cement Association, 1999) and featured a lattice-work of hoop iron embedded in the floors (Stanley, 1979) and the original flat roofs (British Cement Association, 1999). Tall's Patent Shuttering began to gain a reputation which spread to France, where he was awarded a gold medal at the 1867 Paris Exhibition and attracted the attention of Napoleon

III who employed Tall's patent, under licence, when constructing his workmen's flats – the Cités Ouvriéres (Collins, 1959). Tall's shuttering system was later improved by Charles Drake who had been employed as Tall's manager until he realised the advantages of exchanging the timber uprights in the system for metal ones and subsequently patented his own system, leaving Tall to start his own competing firm (Collins, 1959).

As the second half of the 19th century progressed, the economical and fire-resisting properties of concrete became very desirable; particularly for industrial buildings where it was predominantly used in reinforced concrete floors in mills (British Cement Association, 1999), warehouses and other public buildings which were frequently destroyed in expensive, and often fatal, fires (Bussell, 2001b). Concrete architecture also began to attract the attention of the wealthy (Stanley, 1979) and a number of stately homes were built from concrete during this period (British Cement Association, 1999). Some examples include the Fernlands Villa, Chertsey – built by Drake in 1870 (Collins, 1959) – Down Hall, Harlow – completed by Drake in 1873 (British Cement Association, 1999; Stanley, 1979; Collins, 1959) – and Ardtornish Tower in Argyllshire, part of an entire estate built of concrete – created by wealthy industrialist Octavius Smith between 1885-91 (British Cement Association, 1999). However, as concrete construction was particularly vulnerable to poor workmanship (Collins, 1959) and reinforced concrete design was not fully understood, a series of failures in concrete structures led to a tightening in the approval of the Metropolitan Board of Works and eventually resulted in modifications to the existing by-laws (Collins, 1959).

2.3.1.4 William Ward

It was not until the 1870s that any real progress was made in the development of reinforced concrete as a structural material in Britain and, ironically, this was as a result of tests carried out by American inventors. In 1871 William E. Ward, a mechanical engineer from Philadelphia (Collins, 1959), began to conduct experiments using reinforced concrete in preparation for the construction of his own entirely fireproof mansion. Ward cast a series of concrete beams that were reinforced with iron joists and was able to determine their deflection, shear strength, resistance to fire and the optimum size for stone aggregates (Collins, 1959), as well as recognising that composite beam recovered elastically when the load was removed, and that manner of the concrete shrinkage was controlled by the iron (de Courcy, 2001). His most important conclusion, however, was that placing the iron reinforcement at the bottom of the beam was most

effective in utilising the strength of the iron (Collins, 1959) – recognising that an inverted T-section was more efficient than an I-section (de Courcy, 2001).

2.3.1.5 Thaddeus Hyatt

Another American inventor, Thaddeus Hyatt, came to Britain in the early 1870s and filed over 40 patents (Hurst, 2001) relating to pavement lights and concrete flooring. Hyatt employed Dr David Kirkaldy to carry out a series of tests on reinforced concrete beams, with the objective of determining "*a possible means of obtaining cheaper and more reliable fireproof construction than those in common use*" (Hyatt, 1877), and these experiments were described and discussed in his privately circulated publication *'An account of some experiments with Portland-cement-concrete combined with iron, as a building material, with reference to economy of metal in construction, and for security against fire in the making of roofs, floors, and walking surfaces'*. Hyatt determined that reinforced concrete beams could be designed, within reasonable limits for cost and thickness, to withstand the "fiercest flames" and "hottest fires" for between 3 and 48 hours, but that the iron reinforcement required adequate concrete cover on all sides in order to grant the desired fire-resisting properties (Hyatt, 1877).

2.3.1.6 Joseph Monier

The reinforced concrete plant pots made by French engineer Joseph Monier in 1849 (Stanley, 1979; de Courcy, 2001), and patented in 1867, have previously been mentioned. However, these were not Monier's only contribution to the development of reinforced concrete. For many years Monier employed his patent solely in France, using it not only for plant pots, but also for tanks, ponds, floors and, later, for small bridges (Marsh, 1904). This eventually resulted in his 1877 patent for structural reinforced concrete (Newby, 2001) – intended to be used for beams and columns in roads and railways (Collins, 1959). Monier took this system to the 1879 Antwerp exhibition where it was noticed by G. A. Wayss who bought the German patents and formed G.A. Wayss & Co of Berlin and Frankfurt to work them (Marsh, 1904).

Wayss ordered a thorough study of the reinforcing system, which clearly showed its advantages and allowed a set of application principles to be derived (Marsh, 1904). Following on from this Wayss published, in 1887, *'The Monier System (Iron Skeleton with Concrete Filling) in its application to Buildings'* while continuing to develop reinforced concrete in Germany and, although most of the German's reinforced concrete was used for engineering works in France, Germany very quickly established itself as the

lead in the theoretical field, where the most important contributions were made towards future technical developments (Collins, 1959).

2.3.1.7 François Hennebique

Despite all these developments in reinforcing it was not until after 1890 that concrete was used in Britain for building frames (Hurst, 2001), having previously only been used for slabs, lintels and occasionally walls. This was soon to change though as, in 1892, François Hennebique obtained a British patent for his system (Addis & Bussell, 2003) – the first system to be widely used in Britain.

Hennebique was born into a peasant farming family in 1842 at Neuville St. Vaast, but at the age of eighteen he began to work as a mason in the nearby town of Arras where, within seven years, he progressed so rapidly that he was able to establish a building firm of his own (Collins, 1959; McBeth, 1998). The firm carried out a number of important contracts, most of which involved restoring mediaeval cathedrals in northern France, giving Hennebique a wealth of experience in both timber frame design and the management of his workforce. His first recorded use of concrete was during his construction of a friend's villa in 1879 (Collins, 1959) when, as a result of a fire in neighbouring property, Hennebique was prompted to replace the timber joists with pre-cast concrete beams. Following this, he spent over a decade developing his system of frame construction before taking out patents in Belgium and France in February and August of 1892 (Collins, 1959), and establishing himself as a consulting engineer.

Hennebique's patented building system was essentially a frame with infill floor slabs and external cladding in brick, stone, concrete or glass (Newby, 2001). However, in order to secure a patent, the reinforcement had to be distinctively different from other existing profiles and needed to incorporate specific features (Addis & Bussell, 2003). This served Hennebique well as he selected cheap, readily available round, plain mild steel bars which fishtailed at the ends to provide the required anchorage, with flat strip mild-steel links wrapped around the tension bars in the compression zone to provide shear resistance (Addis & Bussell, 2003).

His methods of calculation and typical reinforcement details were given in his patents which helped to satisfy architects and enabled them to develop their designs in line with his patents. Hennebique trained his own engineers and established a technical office in Paris, originally working with only two engineers (Cusack, 2001) – unaware that over the

next three decades, before his death in 1921, he would go on to train many young engineers, leaving a legacy of educated engineers who would go on to develop their own practices (McBeth, 1998).

One of Hennebique's early tasks as a consultant was to underpin the Tower of Notre Dame de Brebieres at Albert, which had undergone large settlements during construction. While all piles manufactured at that time were made of timber, Hennebique designed some reinforced concrete piles which he tested extensively before putting to use. He successfully stabilised the tower (McBeth, 1998) and, in 1897, was granted a patent for his innovative precast reinforced concrete piles that others were quick to adopt (Addis & Bussell, 2003).

As the growing number of commissions came in, Hennebique had great success where many others had failed and this can, in part, be attributed to the way he structured his company. Wisely, he affiliated himself to several trusted and well-established contractors, granting them access to operate his patents on the understanding that these agents followed his strict specifications regarding methods and supervision of work (Collins, 1959). Originally all calculations were carried out by Hennebique's own engineers in Paris but, due to the growing demand, these were later carried out by his agents in their own offices before being sent to Paris to be checked (Newby, 2001). This company structure was of mutual benefit to Hennebique and his agents as it allowed the contractors to continue their other business when there were few reinforced concrete contracts to be undertaken, and equally prevented Hennebique from having to sustain a large workforce during these times, while still ensuring the availability of a skilled workforce when required (Collins, 1959).

While many of Hennebique's early successfully framed structures were in France - including a refinery in Paris in 1894, a spinning mill in Tourcoing in 1895 (Bussell, 2001b; Collins, 1959), a spinning mill near Lille in 1896 and a flour mill at Nort in 1898 (Collins, 1959), he also completed a framed factory in St Michel, Switzerland and another in Cairo in 1895 (Cusack, 2001). Following a further British patent in 1897, Hennebique appointed L.G. Mouchel as his agent in Britain to operate from offices in Victoria Street, Westminster (Bussell, 2001b) – joining Hennebique's expanding organisation which by then consisted of 17 offices, 56 engineers and 55 licensed contractors (Cusack, 2001)

Prior to working for Hennebique, Mouchel had moved his hometown of Cherbourg to Briton Ferry, South Wales, where he began work as a mining engineer during a time when

there was a lively coal trade between France and South Wales (Cusack, 2001) and he was able to establish himself as a prospering businessman. He was acquainted with the directors of Weavers & Co and, upon learning that they wanted to expand their business and construct a second flour mill in Swansea, convinced them to consider using reinforced concrete (Stanley, 1979). As a result of Mouchel's input, Weaver & Co sent their architect to France to study Hennebique's work and upon his return, their directors were unanimous in their selection of his system.

The contract for the mill was signed on 20 October 1897 (Stanley, 1979) and marked the start of Hennebique's first building project in Britain (Bussell, 2001b). He was clearly eager to win the contract and establish his work in Britain as his bid for the work was a mere £4150 (Stanley, 1979), but must have also been aware that his future success in Britain hinged on the success of the project. This is evident from the particular care that was taken in the design and construction of the mill, with the working drawings being completed in his office in Nantes, and the fact that all the sand and steel was transported from Nantes along with experienced French workmen to assist in the project (Cusack, 2001). However, it seems Hennebique was too ambitious and four days before his 30 May 1898 deadline the roof was still not completed (Stanley, 1979). The final load tests were eventually carried out by Mouchel on 1 August 1898 and, despite the delay, Weaver & Co were obviously very satisfied with the work as they commissioned Hennebique to construct a series of grain silos adjacent to the mill which, although similar in size to the previous contract, was quoted at the much higher price of £15,478 (Stanley, 1979).

Hennebique's international empire continued to grow – aided by a considerable amount of work for the 1900 Paris Exhibition including pavilions, bridges, and sewers, which displayed his constructions to the rest of Europe, highlighting the great potential for reinforced concrete both in engineering and architectural use (Newby, 2001). In 1902, only 10 ten years after starting his company, Hennebique was handling over 1500 contracts a year and directing an international company which had licensed contractors in almost every country in Europe (Collins, 1959). By 1909, his system had been used in almost 20,000 structures and the company had 62 offices across four continents – 43 in Europe, 12 in the USA, four in Asia and three in Africa (Bussell, 2001b).

Although there were only seven Hennebique framed buildings built in Britain between 1897 and 1899, the demand had rapidly risen by 1908 to the point that there were 40 new buildings commissioned or in construction in that year alone – bringing the total in Britain

to 130 (Cusack, 2001). The impact of the Hennebique-Mouchel partnership was strong on the British infrastructure, encompassing more than just public and industrial buildings, with L.G. Mouchel & Partners also responsible for constructing almost all of Britain's earliest reinforced concrete bridges – 33 of which were completed before the end of the First World War (Chrimes, 2001), as well as viaducts, tanks, reservoirs, colliery works, marine and river structures, and even boats.

2.3.2 Other Proprietary Systems Used In Britain

The first decade of the 20th century saw the development of many different reinforced concrete systems, most of which originated abroad and had varying degrees of commercial success – the Hennebique and American Kahn system proving to be the most popular in Britain (Addis & Bussell, 2003).

The Kahn bar, introduced by Julius Kahn of Detroit, Michigan in 1903 (Marsh & Dunn, 1909), was used widely in America and Britain by the Trussed Concrete Steel Company (later known as Truscon). It was of unusual profile as it was a square section with two projecting strips that were on diagonally opposite corners and were slit so that they could be bent up diagonally in short lengths, to be anchored in the compression zone of the concrete to form shear reinforcement (Addis & Bussell, 2003; Bussell, 2001b). The resulting beam acted as a truss (a fact that was highlighted in the company's name) and the inclination of the shear reinforcement at approximately 45° reportedly gave an improved shear resistance over similar reinforcements placed vertically (Marsh, 1904).

Edmund Coignet, son of François Coignet, continued his father's work and presented a paper to the French Society of Civil Engineers in 1894. It described his calculations on the modular ratio method which assumed that plane sections remained plane, concrete did not carry tensile stress and that capacity was dictated by limiting stresses under service load (Bussell, 2001b). In 1905 he set up a branch in London and filed a number of patents for beams, floors, walls and even reinforced concrete piles – of which he was one of the first to file a patent (Marsh & Dunn, 1909). His reinforced concrete beams featured round bars and always had double reinforcement – of which the lower reinforcement bars had a greater cross-sectional area than those in the upper section. These were connected to the floor slab with stirrups which were often twisted together over the upper bars to tie them and the lower bars together (Marsh & Dunn, 1909).

One of the few reinforced concrete systems originating in Britain was patented by A.E. Williams of Dagenham Docks, Essex. His system used reinforcement built-up from a series of straight, rolled sections on the top and bottom, connected by two pairs of inclined ties of flat bars on edge, which are riveted or bolted to them with a spirally-wound hooping of wire sometimes added (Marsh & Dunn, 1909).

2.3.3 Changes in Design, Practice and Legislation

Prior to 1915, there had been no statutory regulations for concrete (Addis & Bussell, 2003) and concrete specialists had their own requirements for designs, drawings and schedules – which simply had to satisfy the occasional independent consultant, and construction was carried out by the specialists themselves or by licensed contractors with careful supervision from the specialists (Bussell, 2001b).

Although there had been several studies published on the behaviour of reinforced concrete, such as those by Hyatt, Wayss and Coignet that have been previously mentioned, the first British textbook on reinforced concrete appeared in 1904 and was written by Charles Fleming Marsh (Marsh, 1904; Bussell, 2001a). In it, Marsh described the various proprietary systems that had been developed in Europe and America, as well as structural theory and calculations.

The formation of the Concrete Institute in 1908 brought together, for the first time, all those in Britain with a professional interest in reinforced concrete and provided a forum for the exchange of knowledge. Despite this, the design of reinforced concrete structures was still very much in the hands of a few specialist consultants.

However, this all changed when the 1915 Reinforced Concrete Regulations were introduced, and technical information and experience became widely available to designers and contractors for the first time (Addis & Bussell, 2003), with public access to an acceptable method of designing reinforced concrete (Bussell, 2001b).

Table 2-14 – Summary of the chief characteristics of various systems of reinforced concrete beam construction adopted in Great Britain

NO.	Name Of System	Form Of Tension Bars	Form Of Compression Bars	Form Of Shear Reinforcement	Method Of Fixing Shear Reinforcement	Direction Of Shear Reinforcement
1	Coignet	Round straight bars	Round straight bars	Round rods bent to U-shape	Looped under tension bars and twisted above compression bars	Vertical
1A	Coignet	Round straight bars and round bars bent up near supports	Round straight bars	Bent-up ends of extra tension bars	Continuous with extra tension bars	Diagonal
2	Considère	Round straight bars and round bars bent up near supports	Round straight bars	(a) Bent up at ends of extra tension bars and (b) round rods lapped round the main tension and compression bars	(a) Continuous with extra tension bars and (b) bent round tension and compression bars	(a) Diagonal (b) Vertical
3	Hennebique	Round straight bars and round bars bent up near supports	Round straight bars	Steel strip bent to U-shape and made with spring clip	Sprung on to tension bars and bent over for anchorage in concrete	Vertical
4	Improved Construction	Round straight bars and round bars bent up near supports	Round straight bars	Round rods wound around the main tension and compression bars	Bent round tension and compression bars	Spiral
5	Indented	Corrugated square bars, bent up near supports	Corrugated square straight bars	Bent-up ends of tension bars	Continuous with tension bars	Diagonal
6	Johnson	Round straight bars woven with wire lattice	-	Trough of wire lattice with rectangular or with diamond mesh	Woven with tension bars	Vertical or diagonal strands, according to mesh used
7	Kahn	Square bars generally straight, sometimes bent up towards supports	Square straight bars	Wings attached to the main part of tension and compression bars	Continuous with tension and compression bars	Diagonal
8	Ridley-Cammell	Angle bars straight, and corrugated sheeting	Angle or other bars straight	Troughs of corrugated sheeting	Riveted or bolted	Continuous plate
9	Wells	Twin round bars connected by short web	Round straight bars	Steel strip hangers and bonders	Bent round tension bars	Vertical
10	Williams	Rolled steel sections, straight	Rolled Steel sections straight	(a) Rolled bars (b) Rolled steel sections (c) Spiral coils of steel wire sometimes used in addition	(a) Ends split for anchorage in concrete (b) Riveted or bolted to tension and compression bars	(a) Vertical (b) Diagonal (c) Spiral

Source: Concrete and Constructional Engineering (1908)

2.3.4 Concrete Mix Design

By 1915 the basic mix design for reinforced concrete was 1:2:4 of cement, sand and coarse aggregate, respectively (Yeomans, 1997; Abrams, 1922), with mix proportions of 1:1:2 and 1:1.5:3 also common (Somerville, 2001; The Concrete Society, 2009b). However, many of the specialist contractors had their own mix designs which they would specify for use with their reinforcement systems, as shown in Table 2-15:

Table 2-15 – Mix specifications of various contractors

COMPANY	CEMENT	SAND	COARSE AGGREGATE
BRC	6.5 cwt	13.5 ft^3	27 ft^3
Truscon	1 part	1.5 parts	2.5 parts
Hennebique	1 bag (224 lbs)	4.5 ft.	9 ft.
Considère	5.5-7 swt	11.5 ft^3	23 ft^3
British Steel	1 part	5 parts	-
Coignet	3 parts	5 parts	10 parts
Expanded Metal	1 part	2 parts	4 parts
for floors and walls, from:	1 part	1.25 parts	2.75 parts
to:	1 part	1.75 parts	3.25 parts

Source: Yeomans (1997), original data from Institute of Civil Engineers (1910)

While Portland cement was the base material for historic concrete mixes, the chemical composition and quality would have varied significantly depending on the manufacturer, the available raw materials and the technology available, as previously discussed. Similarly, the composition and size-grading of aggregate was extremely variable, due to variations in local geology and the technology available to crush rock into a particular size. However, Yeomans (1997) reports that there was some consideration of aggregate types for specific purposes.

For example, if the concrete was to act as a filler in a floor, lightweight aggregates which combined the qualities of lightness, strength and resistance to fire – such as coke breeze or broken brick – were preferred. Additionally, coke breeze had the benefit that it could accept nailing, and timber floors could therefore be fixed to concrete slabs containing it (Yeomans, 1997).

By the start of the 20th Century the effects of aggregate size and grading were also being considered by engineers, and, following significant testing on concrete to determine how the grading of aggregates could be adjusted to provide the maximum workability and

strength with minimal segregation, Fuller and Thompson (1907) published work on the subject which would form the foundation of the future approach to the selection of aggregate grading – a subject which will be addressed in more detail in Chapter 6.

With regards to water content, the relationship between the water/cement ratio (w/c) and durability has, historically, not been well understood, and this is shown in the varying approaches to concrete mix designs which were very imprecise. For example, Hennebique required a 'plastic' mix which could be rammed, BRC described their mix as 'slightly wet', the Expanded Metal Company had no requirement for 'wetness', and Truscon specified a 'wet mix' (Yeomans, 1997). In general, it would seem that American engineers specified 'wetter' mixes than was usual in Europe – possibly due to concern that 'dry' mixes gave poor adhesion between the steel and concrete (Yeomans, 1997).

By the 1920s the effects of water content and, more specifically, w/c, were only just beginning to be understood, as shown by a series of investigations carried out at the Lewis Institute, Chicago (Abrams, 1917; Abrams, 1919; Abrams, 1922; Abrams, 1924; Abrams, 1927) which examined the effects of water content, w/c, compaction and water quality on the properties of concrete.

Writing in his 1924 paper, '*Proportioning Concrete Mixtures'*, Abrams reflects on the position of the construction industry on w/c at that time:

> *This brings us to a point which is generally overlooked in our building codes and other documents of that kind. It seems to be the opinion that increasing the quantity of cement is the cure for all the difficulties of weak or inferior concrete. However, if adding cement is not at the same time accompanied by a reduction in the water-ratio, it does not accomplish any useful purpose. The water-ratio may be changed due to changes in the relations of the quantity of cement, grading of aggregate, or changes in relative consistency of the concrete; however, we arrive at the same result, indicating that the water-ratio is the thing that actually controls the strength and other properties of concrete…*
>
> *I know that a great many people are sceptical as to the practicability of such control; some may still doubt whether an excess of water does produce an inferior concrete; but I can say with all the emphasis of which I am capable that I am very sure it does, and that in many cases the concrete produced on the job has a strength of probably not more than 20 to 30% of the strength it should have, and*

> *probably not more than 60 or 70% of the strength upon which the design was based. So, under these conditions we should not be surprised to find inferior concrete, and we do find it too often.*

While the observation that the effects of w/c were not appreciated is unsurprising, a revelation from Abrams' paper comes from his comment that, *"The usual water-ratio for ordinary conditions is about 0.8 or 0.9, or about 6 to 6-3/4 gal. per sack of cement"*. This is of concern due to the implications that high w/c, such as these, have on the durability of concrete due to the increase in the number and interconnectivity of capillary pores in the cement paste that result (Neville, 2001).

Despite the, seemingly, common use of 'high' w/c at that time, Abrams (1924) shows that there is some understanding of the relationship between w/c and durability, when he writes:

> *A great deal has been said with reference to the compressive strength of concrete and we have come to accept the compressive strength as a measure of the other desirable qualities of concrete. The strength of concrete is an important factor in building construction and in other types of construction; however, the quality of concrete has a wider bearing than strength. A structure which is exposed to the weather, with wide ranges of temperature, wide variations in moisture content, and probably exposed to other destructive agencies, must have a very considerable degree of resistance if it is to give a good account of itself. That is entirely aside from the matter of strength. It is true, however, that the strength of concrete reflects to a very large degree the ability of concrete to withstand these other agencies.*

Unfortunately, Abrams understanding of the relationship between w/c and durability is overshadowed by his conclusion that, *"we may consider that the compressive strength of concrete is an entirely satisfactory measure of its quality,"* as, for normal mixes, w/c – not compressive strength – is now considered the dominant parameter affecting the durability of concrete (The Concrete Society, 1999). Moreover, there are several other important factors relating to concrete quality which will affect durability to such a degree that compressive strength alone cannot be considered an entirely satisfactory measure of quality, and these will be discussed in subsequent sections of this report.

2.4 DETERIORATION OF CONCRETE

Concrete is a complex, heterogeneous material which degrades over time, both physically and chemically, depending on its environment and manufacture quality. In modern construction, the deterioration mechanisms of concrete are relatively well understood and are addressed at the design stage by the current building codes and engineering standards, which ensure that concrete is manufactured in such a way that it is suitable for its environment, and provides satisfactory performance during its service life. However, this has not always been the case and, as a result, many concrete structures suffer from extensive deterioration which could have been minimised or, in some cases, avoided altogether.

2.4.1 Corrosion of Steel Reinforcement

The release of alkalis during the hydration of cement results in a highly alkaline environment, with the pore solution initially higher than pH 13 and lowering to around 12.5 (the pH of a saturated solution of calcium hydroxide) in most mature conventional concretes (Building Research Establishment, 2004a). This alkaline environment is protective for the steel as it enables the formation of a thin passivating oxide layer on the surface of the steel (Building Research Establishment, 2004a), which prevents the reinforcement from reacting with water and oxygen, eliminating the risk of any corrosion occurring (Neville, 2011). However, breakdown of the oxide layer can occur if chlorides are present in the area around the steel or if the pH of the surrounding pore solution falls as a result of carbonation, resulting in a loss of protection which allows corrosion of the reinforcement to occur. Once the breakdown of the oxide layer has occurred, the rate of corrosion is dependent upon the supply of oxygen and degree of moisture present around the steel (Building Research Establishment, 2004a).

The corrosion of the reinforcement is an electrochemical reaction in which the iron atoms lose electrons and flow as ferrous ions – creating an anode. The electrons produced in this self-sustaining reaction flow through the reinforcement to cathodic sites, and there they react with oxygen and water from the outside to produce additional hydroxyl ions, $(OH)^-$ (Broomfield, 2003). The soluble ferrous ions then react with these hydroxyl ions to form ferric hydroxide which, as a result of further oxidation, is converted to rust (Neville, 2011). The reactions involved in the corrosion process are shown below (Broomfield, 2003; Neville, 2011) and in Figure 2-3:

Anodic reactions:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (14)$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad \text{[ferrous hydroxide]}$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \quad \text{[ferric hydroxide]}$$

$$\rightarrow 2Fe_2O_3.H_2O + 4H_2O \quad \text{[Rust]}$$

Cathodic reaction:

$$1/2O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \quad (15)$$

The formation of this solid rust causes a volume increase which leads to cracking in the surrounding concrete (Broomfield, 2003), and corrosion of steel reinforcement is often characterised by cracks running parallel to either the main reinforcement bars or to the stirrups. Where cracks coincide with reinforcing bars, as shown in Figure 2-4, a greater proportion of the bar is exposed to moisture and oxygen – resulting in anodic and cathodic areas that are relatively equal in size. When this is the case it typically leads to generalised corrosion and further cracking as a result of the expansive forces produced (Building Research Establishment, 2000a) and if no action is taken to prevent the progression of the corrosion, spalling of the concrete will occur (Everett & Treadaway, 1980).

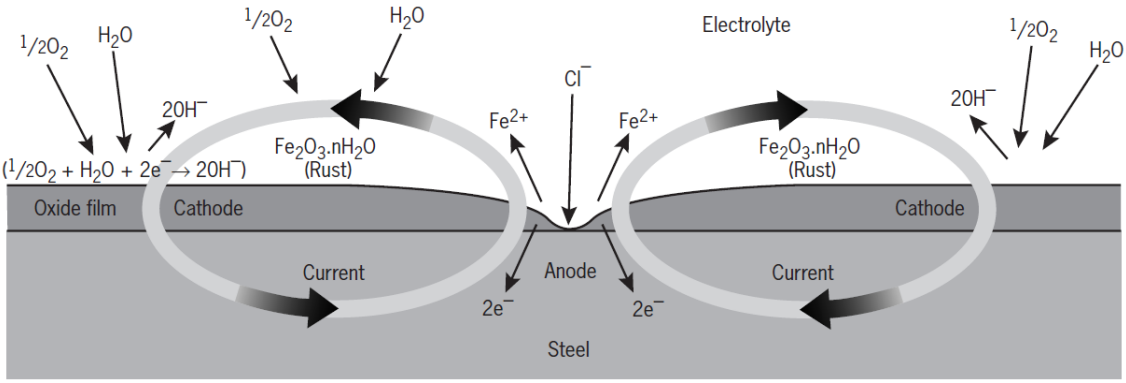

Figure 2-3 – The mechanism for pitting corrosion, reproduced from Digest 444 Part 1 (Building Research Establishment, 2000a)

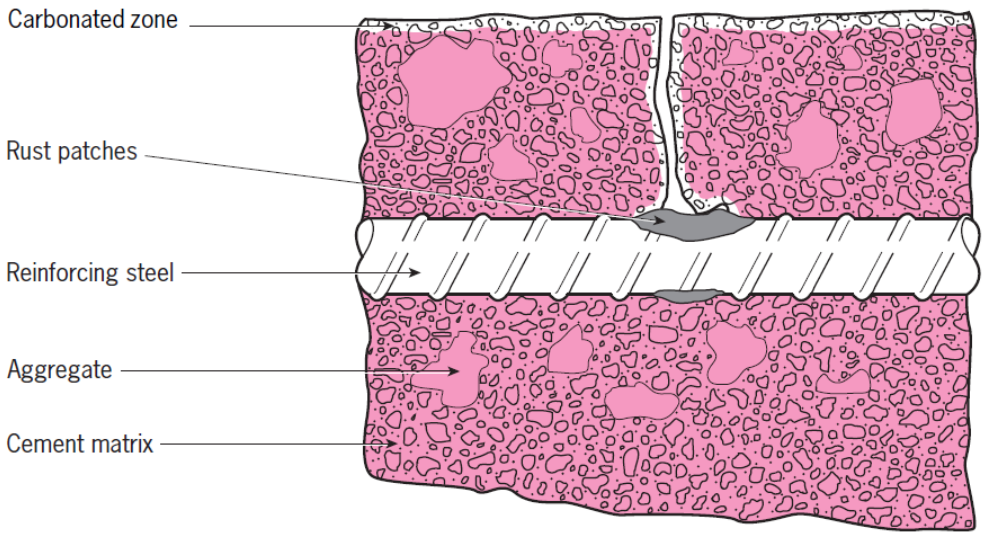

Figure 2-4 – Diagrammatic view of steel corroding in cracked concrete (Building Research Establishment, 2000a)

2.4.1.1 Chloride Induced Corrosion

There are two ways in which chloride ions can enter concrete. They may be added to the fresh concrete during mixing, either as an aggregate contaminant or as part of an admixture, or they may enter the hardened concrete from an external source (Lambert, 2002). However, the risk of cast-in chlorides is of greater concern in historic concrete structures than in modern concrete structures since the use of calcium chloride in concrete admixtures – primarily set accelerators (Building Research Establishment, 2000b) – was banned in 1976 and the contamination of aggregates now has enforced limits (Bamforth, *et al.*, 1997).

While the risk from cast-in chlorides is relatively low in modern structures, chloride induced corrosion is still a primary durability concern in the United Kingdom, regardless of structure age, due to the high risk of external ingress of de-icing salts from roads and vehicles, and sea-salt ingress from marine environments (Broomfield, 2003; Bamforth, *et al.*, 1997). Furthermore, corrosion is most severe when the chlorides penetrate from an external source at the intersections of reinforcement bars and cracks, as the anodic zones are relatively small (Building Research Establishment, 2000a). When this occurs, localised corrosion can cause very large, even total, loss of cross-sectional area of the steel at these zones, while the same reinforcement bars can remain completely corrosion-free just outside of these zones (Building Research Establishment, 2000a).

Cracks caused by chloride induced corrosion can be distinguished from normal service cracks, which reach widths up to about 0.3 mm (Building Research Establishment, 2000a), as they are wider than hairline and usually taper from the point of corrosion, with

rust staining and/or local bulging of the concrete often visible (Building Research Establishment, 2000b). In the event that chlorides are concentrated near the surface of the steel, or that access to water and oxygen is limited to a single location on the steel, localised pitting corrosion can occur – causing severe loss of cross-sectional area in a single location while the rest of the bar remains free from corrosion (Building Research Establishment, 2000b).

2.4.1.2 Carbonation

Carbonation is an inevitable form of concrete degradation and, as it is time-dependent, it is of particular relevance to historically significant structures. As previously mentioned, reinforcement within concrete is protected by a thin passivating oxide layer on the surface of the steel which prevents it from corroding. This layer is self-sustaining and self-maintaining indefinitely, providing the surrounding pore solution stays above pH 11 without contamination (Broomfield, 2003). However, carbon dioxide (CO_2) in the atmosphere combines with moisture to form carbonic acid which then reacts with calcium hydroxide ($Ca(OH)_2$) and other alkaline hydroxides in the pore water, resulting in a reduction in the alkalinity of concrete (Lambert, 2002) to a pH of around 8 (Broomfield, 2003). This neutralisation of the alkalinity, known as 'carbonation,' causes the breakdown of the passivating oxide layer – allowing corrosion to occur.

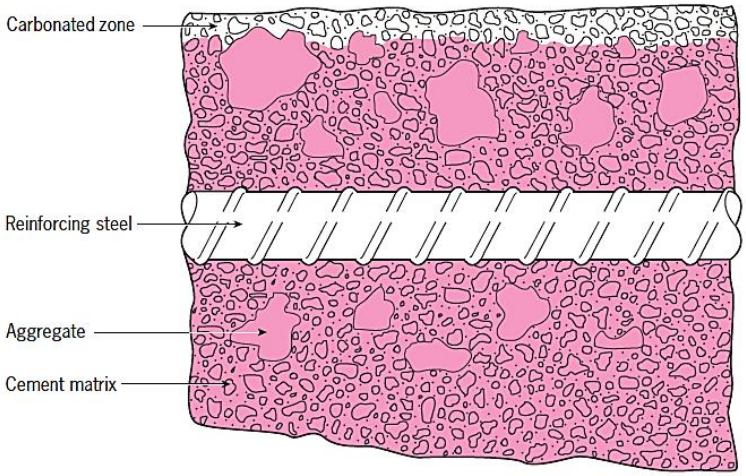

Figure 2-5 – Diagrammatic view of steel protected from carbonation-induced corrosion in partially carbonated concrete, reproduced from Digest 444 - Part 1 (Building Research Establishment, 2000a)

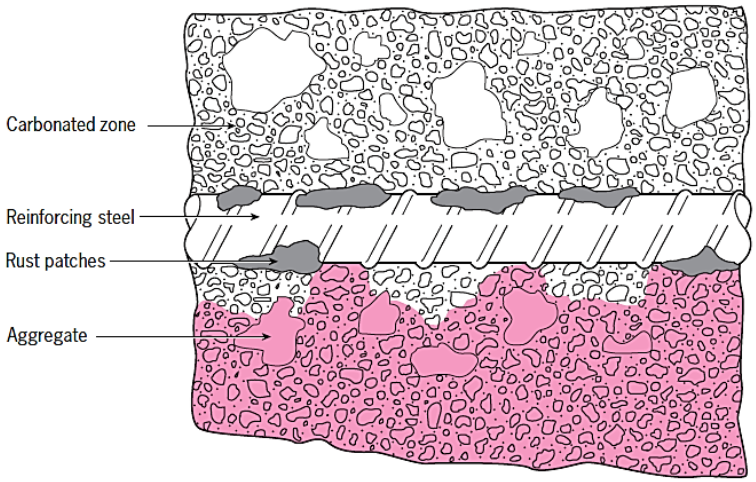

Figure 2-6 – Diagrammatic view of steel corroding in carbonated concrete, reproduced from Digest 444 - Part 1 (Building Research Establishment, 2000a)

Carbonation takes place very slowly over many years, with typical Portland cement concrete potentially carbonating to a depth of 5-8 mm over a 10 year period, and increasing to 10-15 mm after 50 years, with the rate of increase in carbonation depth generally decreasing the longer the concrete is exposed to air (Building Research Establishment, 1995). This decrease in rate can be attributed to the fact that CO_2 has to diffuse from the surface through the already carbonated pore system (Neville, 2011). While corrosion as a result of carbonation should not occur during the lifetime of a structure, provided that the cover depth and concrete quality are correctly specified for the exposure conditions (The Concrete Society, 2008), historically-significant structures may suffer from carbonation induced corrosion as result of inadequate design, poor construction practice or simply from the fact they have long exceeded their intended lifespan.

The depth of carbonation of concrete in dry, internal conditions is roughly proportional to the square root of the duration of exposure and can be expressed by the following equation (Building Research Establishment, 1995; Neville, 2011):

$$D = k\sqrt{t} \qquad (16)$$

where:

D is the depth of carbonation in mm;

k is a constant related to concrete quality and environmental conditions;

t is time of exposure in years.

While the depth of carbonation is generally limited to the surface of the concrete, there are several factors which affect the rate and depth or carbonation. These can be divided into two categories: *concrete quality issues* and *environmental conditions*.

Water/cement ratio (w/c) plays a critical role in the quality of concrete and, for normal mix design, can be considered the dominant parameter affecting the durability of concrete (The Concrete Society, 1999). This is because an increase in w/c ratio results in a higher percentage of capillaries and other voids within the cement matrix (Ishai, 1968) – creating a concrete that is both more porous, and with lower alkali reserves to resist the neutralisation process (Broomfield, 2003). To put the importance of water/ratio into perspective, carbonation that could reach a depth of 15 mm after 15 years in a concrete with a w/c of 0.60, would take 100 years to reach the same depth if the concrete had a w/c of 0.45 (Neville, 2011).

Carbonation can also penetrate further as a result cracking, which provides a pathway for ingress, as shown in Figure 2-4 (Building Research Establishment, 2000a), or as a result of construction defects, which result in low-quality concrete cover.

2.4.2 Design and Construction Defects

While a significant number of cases of premature degradation are attributed to poor workmanship (Harrison, 1999), many of the flaws attributed to the contractor actually result from a lack of understanding of construction operations by the designer (Hoff, 1999).

2.4.2.1 Inadequate Cover to Reinforcement

Inadequate cover is the most common cause of corroding reinforcement (The Concrete Society, 2008), as the lack of sufficient cover invariably results in areas with a high risk of corrosion due to both carbonation and chloride ingress (Lambert, 2002). Although inadequate cover is a problem often associated with the construction phase, attributed to incorrect reinforcement placing and shuttering, it can also be a result of a deficiency in the design. This is often the case in historic concrete structures, as older design codes did not specify adequate cover and designers would also specify cover to the main steel and not to any additional steel, such as stirrups (Broomfield, 2003).

2.4.2.2 Poor Compaction

Air becomes entrapped in fresh concrete as a result of mixing, transportation and placing, and this results in the formation of voids which need to be removed to prevent an increase

in the permeability of the hardened concrete. The volume of entrapped air in fresh concrete varies depending on the consistence class – for example, an S2 concrete may contain over 5% entrapped air, while an S1 concrete may contain up to 20%, which is a significant problem as the voids formed reduce the strength of the concrete by more than 5% for every 1% of entrapped air (The Concrete Society, 2008). Poor compaction can also lead to honeycombing at shuttered faces which not only results in a relatively weak concrete but also reduces the depth of cover to reinforcement. As such, it is essential for the durability of concrete to ensure that as much air as removed as possible.

2.4.2.3 Segregation & Bleeding

Segregation in fresh concrete is a significant factor which contributes to an increase in the variation in the composition of the hardened concrete. It can be attributed to several factors including over-compaction, poor placement and inadequate mix design – the latter is particularly relevant to historic concrete as the first standards for concrete in the UK were not introduced until the first half of the 20th century and even then little attention was paid to the effects of particle size distribution.

A lack of suitable grading is conducive to segregation, which in turn can result in the coarse aggregate settling to the bottom of the mix and the cement paste rising to the top (Neville & Brooks, 2010). The effects of segregation on concrete heterogeneity should not be underestimated, particularly when selecting samples for analysis, as it has been found to result in a difference in cement content of as much as 100 kg/m^3 between the top and bottom of concrete walls and columns (Skinner, 1980)

Bleeding, another form of segregation which occurs in fresh concrete, is usually a result of over-compaction, causing the settlement of solid constituents which displace water from the mix (The Concrete Society, 1999). This can have a detrimental effect as it causes water to rise to the top surface where it accumulates, creating a weak and porous layer in the hardened concrete which varies from the underlying material (Neville & Brooks, 2010). It can also result in areas of high permeability below large aggregate or reinforcement as the rising water becomes trapped; eventually creating voids in the hardened concrete (Neville & Brooks, 2010). Bleeding can also occur at joints in formwork if they are insufficiently sealed – allowing water and fines to escape and resulting in a honeycombed face.

While some bleeding is inevitable, it should be avoided where possible as the resulting areas of poor bond under coarse aggregate or reinforcement and the weak, porous layer at the surface are detrimental to the durability and strength of hardened concrete.

2.4.3 Chemical Degradation

2.4.3.1 Alkali-Aggregate Reaction

Alkali-aggregate reaction (AAR) occurs as a result of the interaction between alkaline pore fluids and reactive minerals in certain types of aggregate (Building Research Establishment, 2004b). There are two main forms of AAR – alkali-carbonate reaction (ACR) and the more common alkali-silica reaction (ASR) (Farny & Kerkhoff, 2007).

ASR causes damage to concrete when the alkaline Na_2O and K_2O from cement reacts with the siliceous material in certain aggregates, forming alkali-silicate gel which absorbs water and consequently increases in volume (Neville, 2011) and, due to the internal stresses and expansion caused by the reaction, ultimately results in cracking (Clayton, 1999). While ASR crack widths can range from 0.1 mm to up to 10 mm, they are rarely deeper than 25 mm and so tend to only affect the appearance and serviceability of concrete (Neville, 2011).

2.4.3.2 Sulfate Attack

Sulfates, which can be found in soil and groundwater – occurring naturally or as a result of industrial applications – react with certain compounds in concrete with detrimental effect. There are two main forms of sulfate attack that occur in hardened concrete, and these can appear separately or together. The first of these occurs when sulfates react with hydration products in concrete to form expansive products, such as ettringite and gypsum, which in turn can cause cracking and surface scaling. The second form of sulfate attack results in the dissolution of the hydration products responsible for cementing the concrete when they are attacked by sulfates, or their decomposition when calcium hydroxide is removed through its own reaction with sulfates (The Concrete Society, 2000).

The type and extent of sulfate attack are dependent on several factors, including the type of concrete, as well as the type and concentration of the sulfate (The Concrete Society, 2000). For example, while calcium sulfate only reacts with the hydrated calcium aluminates to form calcium sulfoaluminate, sodium sulfate reacts with the free calcium hydroxide and forms calcium sulfate which in turn reacts with the aluminates. In the case of attack from magnesium sulfate, the action is even more severe, as it not only reacts

with the aluminates and calcium hydroxide but also decomposes the hydrated calcium silicates – resulting in the rapid formation of gypsum (Eglinton, 1998).

As discussed in Chapter 2.2.1.1, C_3A is susceptible to sulfate attack and so cement with a low C_3A content is beneficial in this regard. However, low C_3A content cement also has a low resistance to chloride ingress and therefore, in some cases – such as exposure to sulfates from marine environments – the use of sulfate resistant cement (with low C_3A content) may result in accelerated chloride induced corrosion (Broomfield, 2003).

2.4.4 Environmental Damage

2.4.4.1 Freeze-Thaw Damage

This type of damage is of particular concern across Scotland, where the mean daily minimum temperature in the coldest months varies locally from -3°C to 2°C (Met Office, 2016) and results in cycles of freezing and thawing. These cycles cause cumulative damage which progresses deeper into the concrete each time water in the pores freezes and expands, creating a pressure higher than the strength of the surrounding material (The Concrete Society, 2000).

Freeze-thaw damage predominantly occurs as delamination of the concrete, known as scaling, in the cement-rich surface layer when the fine, interconnected capillary pores in the cement paste become saturated and freeze (Harrison, *et al*., 2001). This problem is further exacerbated by the use of de-icing salts, which increase the moisture content of concrete prior to freezing, and induce a thermal stress as the concrete cools rapidly a few millimetres below the surface as heat is taken to the surface to thaw the ice – which then provides an additional source of water for further freeze-thaw cycles (Harrison, *et al*., 2001).

Although less common, damage can also occur in the pores of coarse aggregates which, depending on their size and distribution, can allow the development of a high bursting stress during freeze-thaw conditions (Harrison, *et al*., 2001). If aggregate with such a pore structure is located close to the surface and is almost fully saturated, the thin layer of cement paste between the aggregate and the surface is displaced by the expansion – causing a ‘pop-out’ (The Concrete Society, 2000). However, aggregates of this nature are not common in the UK, and those that are tend to be of sedimentary origin (Harrison, *et al*., 2001) which, due to their high-shrinkage capacity – which will be discussed further

in Chapter 2.6.1 – are not permitted for use in reinforced concrete members that are exposed to the weather (Building Research Establishment, 1991a).

In modern construction, the freeze-thaw resistance of concrete is enhanced through the use of air-entraining admixtures which produce small, closely spaced air bubbles which provide room for expansion in the hardened concrete – preventing the build-up of pressure and any consequential damage (The Concrete Society, 2000). These spherical, entrained air bubbles are larger than capillary pores and, as a result of the suction of smaller interconnecting pores, remain free of water (Harrison, *et al*., 2001).

2.4.4.2 Physical Salt Weathering

Physical salt weathering occurs when salts, usually sulfates, but sometime chlorides, ingress into concrete from the ground as a result of capillary action. As these salts crystallise in the pores of the concrete's surface layer they expand – exerting pressure in a manner similar to that of ice forming during freeze-thaw cycles. As such, physical salt weathering results in a similar form of damage, with surface scaling occurring in the cement paste, and the possibility of larger pop-outs occurring when the aggregate has a relatively high porosity, and is consequently also susceptible to ingress (The Concrete Society, 2000).

2.4.4.3 Weathering

As concrete is a porous material, weathering is an inevitable form of deterioration that will occur over time. While the importance of weathering as a characteristic relevant to concrete repair will be discussed in Chapter 2.6.3, the actual mechanisms by which weathering occurs will be discussed separately at this stage.

Concrete weathering is caused by pollution and natural effects, and results in unexpected variations in the appearance of a structure (The Concrete Society, 2000) when wind and gravity cause soiling to be redistributed across its surface in rainwater (The Concrete Society, 2013). There are three predominant architectural factors that dictate the extent of concrete weathering (The Concrete Society, 2013):

1. The overall massing, orientation and geometry of the structure and its relationship to existing buildings and topography
2. The choice of material and the surface finish achieved
3. The detailing which controls the flow of water over a structure's surface

However, the porous, cement-rich surface layer can be intentionally removed from concrete (by acid etching, washing or tooling) in order to reveal a surface which includes exposed aggregate. This often makes the performance of the surface layer easier to predict and control, as the characteristics of the aggregate become as important as those of the cement matrix in determining the surface properties (The Concrete Society, 2013).

Staining

Staining can occur in concrete if, prior to concrete casting, the reinforcement has been fixed in place for some time and rust from the steel gets washed into the formwork by rainwater – resulting in permanent staining of the concrete surface if not removed (The Concrete Society, 2000). Cosmetic staining can also occur on concrete if copper salts or oxides are washed by rainwater onto its surface from copper or bronze features – such as statues, flashing and cladding (The Concrete Society, 2000).

However, in both of these cases, the staining is purely cosmetic and should not be mistaken for staining which results from the corrosion of steel reinforcement within the body of the concrete.

Efflorescence

'Efflorescence' is a general term used to describe white deposits or stains on building materials. (The Concrete Society, 2013). It is used to describe several phenomena, of varying degrees of severity, which occur in concrete as a result of poor workmanship or detailing, and occurs when water percolates through inadequately compacted or poorly drained concrete (The Concrete Society, 2013). The three main forms of efflorescence on concrete are: lime bloom, lime weeping and crystallisation of soluble salts

Lime bloom, is a cosmetic problem characterised by white surface patches or a general lightening of the concrete surface. Lime weeping is more serious and may affect durability, as it occurs when calcium hydroxide is dissolved from the cement matrix and deposited on the concrete surface. Once it reaches the surface it reacts with CO_2 and forms calcium carbonate and, in more severe cases, this accumulation is so large stalactites begin to form (The Concrete Society, 2000). Crystallisation of soluble salts, or 'cryptoflorescence', does not occur as deposits of calcium carbonate, but, instead, consists of soluble salts not normally present in concrete – usually from contaminants present in the original concrete mix, or external sources such as groundwater (The Concrete Society, 2013).

Table 2-16 – Summary of efflorescence types

TYPE	COMMONLY OCCURS ON	CHEMICAL NATURE	CONDITIONS ENCOURAGING APPEARANCE	PREVENTIVE MEASURES	RECOMMENDED REMOVAL METHOD
Lime bloom	Any concrete, but particularly noticeable on coloured concrete and coloured concrete products	Calcium carbonate	High humidity; trapped layers of water	Reduce fines or silt in aggregate; reduce water/ cement ratio; use water-resisting admixture; apply surface treatment; control storage	Wash with acid
Lime weeping	Retaining walls; roof gardens; bridges; multi-storey car parks	Calcium carbonate	Cracks or joints which allow water to pass through	Avoid cracks and poor joints	Chip off
Salt crystallisation	Retaining walls; concrete made with sea-water or with unwashed marine aggregates	Wide range of soluble salts	Use of contaminated aggregates or mixing water; permeable concrete in contact with ground-water	Use clean aggregates and fresh water; provide a waterproof membrane; use good-quality concrete	Brush off; scrub off with water or wash with acid (as appropriate)

Source: The Concrete Society (2013)

Biological Growth

Hardened concrete initially has an alkaline pH of around 13 and this prevents biological growths from becoming established on its surface (The Concrete Society, 2000). However, over time the alkalinity of concrete is inevitably reduced as it reacts with atmospheric CO_2 and carbonation occurs – creating an environment which is suitable for colonisation by micro-organisms such as algae, fungi and bacteria. Over time growths of algae and lichens become visible and, as soiling collects around the colonies, this facilitates further growth of moss and plants (The Concrete Society, 2013).

While biological growths are primarily an aesthetic problem, they also pose a threat to concrete durability in a number of ways. Firstly, the presence of organic material can cause an increase in moisture content at the surface of the concrete as water becomes trapped – resulting in pore saturation even in dry conditions. Secondly, some algae produce cement dissolving acids that will wear away the binder over time and, finally, if plants become established on the concrete their roots can grow into cracks and defects, increasing the stress and resulting in further cracking or spalling (The Concrete Society, 2000).

2.5 METHODS OF CONCRETE REPAIR

Once a concrete structure has been assessed and the causes of deterioration determined, a management plan utilising the following six approaches has to be prepared in order to ensure that all future requirements of the structure are met (British Standards Institution, 2008b):

1. Do nothing for a certain time but monitor.
2. Re-analyse the structural capacity, possibly leading to downgrading in function.
3. Prevent or reduce further deterioration.
4. Strengthen or repair and protect all or part of the concrete structure.
5. Reconstruct or replace all or part of the concrete structure.
6. Demolish all or part of the concrete structure.

There are a wide variety of repair and prevention options available to address the various forms of concrete deterioration discussed in the previous section, the requirements and conformity of which are described in the 10 parts of BS EN 1504 *'Products and systems for the protection and repair of concrete structures – Definitions, requirements, quality control and evaluation of conformity'*. These are summarised in Table 2-17 – principles and methods for protection and repair of concrete, from BS EN 1504-9 (British Standards Institution, 2008b).

In the case of listed structures and buildings, there are additional statutory controls that need to be taken into consideration. Furthermore, the principles of conservation strategy include minimising intervention and protecting the historic and architectural value of a structure. This is of particular relevance to concrete structures, as concrete repair is inherently an invasive process which often cannot be isolated to individual elements in the same manner as other historic structures – such as those built of traditional masonry, as concrete tends to be monolithic in form (Broomfield & Macdonald, 2003).

Table 2-17 – Principles and methods for protection and repair of concrete structures

PRINCIPLE		EXAMPLE OF METHODS BASED ON THE PRINCIPLES	Relevant part of EN 1504
Principles and methods related to defects in concrete			
1. Protection against ingress	1.1	Hydrophobic impregnation	2
	1.2	Impregnation	2
	1.3	Coating	2
	1.4	Surface bandaging of cracks	-
	1.5	Filling of cracks	5
	1.6	Transferring cracks into joints	-
	1.7	Erecting external panels	-
	1.8	Applying membranes	-
2. Moisture Control	2.1	Hydrophobic impregnation	2
	2.2	Impregnation	2
	2.3	Coating	2
	2.4	Erecting external panels	-
	2.5	Electrochemical treatment	-
3. Concrete restoration	3.1	Hand-applied mortar	3
	3.2	Recasting with concrete or mortar	3
	3.3	Spraying concrete or mortar	3
	3.4	Replacing elements	-
4. Structural Strengthening	4.1	Adding or replacing embedded or external reinforcing bars	-
	4.2	Adding reinforcement anchored in pre-formed drilled holes	6
	4.3	Bonding plate reinforcement	4
	4.4	Adding mortar or concrete	3, 4
	4.5	Injecting cracks, voids or interstices	5
	4.6	Filling cracks, voids or interstices	5
	4.7	Restressing - (post-tensioning)	-
5. Increasing physical resistance	5.1	Coating	2
	5.2	Impregnation	2
	5.3	Adding mortar or concrete	3
6. Resistance to chemicals	6.1	Coating	2
	6.2	Impregnation	2
	6.3	Adding mortar or concrete	3
Principles and methods related to reinforcement corrosion			
7. Preserving or restoring passivity	7.1	Increasing cover with additional mortar or concrete	3
	7.2	Replacing contaminated or carbonated concrete	3
	7.3	Electrochemical re-alkalisation of carbonated concrete	-
	7.4	Re-alkalisation of carbonated concrete by diffusion	-
	7.5	Electrochemical chloride extraction	-
8. Increasing resistivity	8.1	Hydrophobic impregnation	2
	8.2	Impregnation	2
	8.3	Coating	2
9. Cathodic control	9.1	Limiting oxygen content (at the cathode) by saturation or surface coating	-
10. Cathodic protection	10.1	Applying an electrical potential	-
11. Control of anodic areas	11.1	Active coating of the reinforcement	7
	11.2	Barrier control of the reinforcement	7
	11.3	Applying corrosion inhibitors in or to the concrete	-

Sourced: Reproduced from BS EN 1504-9 (British Standards Institution, 2008b)

2.5.1 Concrete Restoration

Concrete restoration is carried out using one of two methods: patch repairs or concrete replacement. However, prior to the application of a repair material, any damaged or deteriorated concrete has to be broken out – usually by pneumatic tools or high-pressure water jetting. In the case of reinforcement corrosion, concrete removal has to continue past the reinforcement bars in order for them to be cleaned and treated with a protective coating. The surface of the remaining concrete has to then be cleaned and, in some cases, a bonding aid applied to improve cohesion between the old and new materials (The Concrete Society, 2000).

2.5.1.1 Patch Repairs

Patch repairs are by far the most common repair method, and can be hand-applied, poured or spray-applied depending on the nature and extent of damage, and the area of material that is being repaired. The repair material can be either a cementitious mixture or a proprietary material, but proprietary materials can be significantly more expensive and, while they provide a good-quality, low-shrinkage bond, they often do not visually match the parent material (Broomfield & Macdonald, 2003).

In a review of 230 case histories published by the Building Research Establishment, Tilly & Jacobs (2007) found that patch repairs were applied as part the repair strategy in over 60% of cases. 60% of these repairs were carried out using a cementitious mortar, 30% with a polymer modified mortar and 10% with other specialist repair mortars. However, of these repairs, the cementitious patches had a success rate of only 45% and the polymer modified patches 50%.

2.5.1.2 Concrete Replacement

For larger volume repairs it is common practice to replace the damaged area with new concrete, which is generally poured in vertical members with a thin section, or sprayed on larger areas (The Concrete Society, 2000). In some cases, it is also possible to completely replace individual elements, particular if they are pre-cast.

2.5.2 Barrier and Impregnation Systems

2.5.2.1 Coatings, Blockers and Sealants

While it is not common practice in the UK to coat concrete structures at the time of construction, barrier systems are applied in some cases where concrete is exposed to severe conditions which pose an increased deterioration risk, or as part of a repair strategy

to prevent the progress of deterioration (Broomfield & Macdonald, 2003). In the BRE review of case histories, barrier systems were found to have been used in 35% of repairs and only successful in 50% of these. However, barriers were usually implemented in combination with other methods, such as patch repairs, with only 30% of cases showing the use of barriers as a solo repair method (Tilly & Jacobs, 2007).

There are three main types of barrier used to protect the surface of concrete from the ingress of moisture and harmful agents – each operating in a slightly different way (The Concrete Society, 2000):

- Film forming coatings
- Pore liners/blockers
- Sealants

Film-forming coatings, such as paints and epoxies, provide a physical barrier on the concrete surface. Pore liners/blockers are low-viscosity liquids which either penetrate the pores of the concrete surface and, on solidification, provide a physical plug in the pore, or act as a hydrophobic cover on the surface – altering the wetting characteristics to prevent water, from penetrating the surface under low pressure. Sealants act as an intermediate between the other two methods, as they can contain solvents which allow them to penetrate into the concrete surface, while simultaneously forming a thin, physical barrier on top (The Concrete Society, 2000).

While coatings, blockers and sealants can provide an effective solution in the prevention of deterioration concrete, this is only the case if the correct type of barrier is applied to that particular circumstance. Certain barriers are also unsuitable in structures that have an important aesthetic character, as they alter the colour and texture of the concrete surface. Further guidance on the selection and application of barrier systems can be found in BS 1504-2 (British Standards Institution, 2004) and Concrete Society Technical Report No. 50 '*Guide to Surface Treatments for Protection and Enhancement of Concrete'* (1997).

2.5.2.2 Corrosion Inhibitors

Corrosion inhibitors are a newer, less common form of proprietary concrete protection which have three main forms: Vapour-phase inhibitors which create a molecular layer on steel which prevents corrosion, calcium nitrite applied in a concrete mixture which

acts as an anodic inhibitor, and monofluorophosphate, which is believed to create a highly alkaline environment as it hydrolyses in the concrete (Broomfield & Macdonald, 2003).

2.5.3 Electrochemical Treatments

While the previous methods of repair have been focussed on treating damaged concrete and preventing the ingress of harmful agents through concrete, electrochemical treatments focus on the steel reinforcement – turning it into a cathode by passing a current through it from an artificial anode. Although electrochemical treatments tend to have high initial costs, they are often are more cost-effective in the long-term treatment of structures with a remaining service life of ten years or more (Broomfield & Macdonald, 2003), and in recent years they have become more a popular repair option as engineers have become more confident in their successful use (Tilly & Jacobs, 2007).

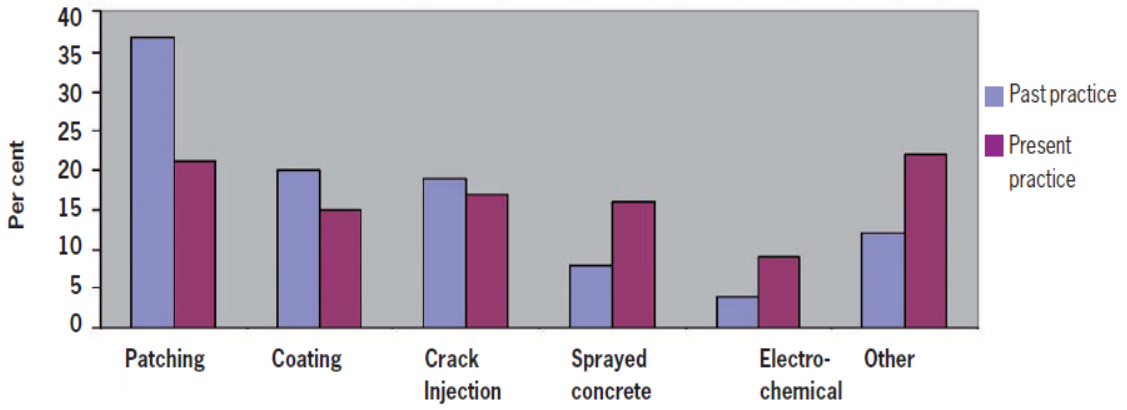

Figure 2-7 – Past and present use of repair techniques, reproduced from Tilly & Jacobs (2007)

2.5.3.1 Cathodic Protection

Cathodic protection (CP) has been used in reinforced concrete structures since the 1970s and more generally in metal structures for almost 100 years (The Concrete Society, 2000). There are two types of cathodic protection; impressed current cathodic protection (ICCP) and galvanic/sacrificial anode cathodic protection. Reinforcement corrosion occurs as a result of the formation of anodes and cathodes on the steel reinforcement as described in Chapter 2.4.1, and cathodic protection can significantly reduce the rate and extent of corrosion by purposefully introducing a separate anode.

ICCP comprises an anode that may initially be inert, but has an applied DC electrical current which forces the steel reinforcement to become negatively charged – promoting the cathodic reaction while reducing the anodic reaction (The Concrete Society, 2011). As well as a DC power supply, ICCP also requires various control circuitry and monitoring devices which result in relatively high initial costs. However, ICCP is a

desirable repair solution for listed buildings or those with a particular aesthetic character that is to be preserved, as it can provide a less invasive repair than more traditional options (Broomfield & Macdonald, 2003).

Galvanic anode cathodic protection requires an anode of a more reactive metal, such as aluminium, zinc or magnesium alloy, and, in some cases, a DC power supply and monitoring devices. It works in much the same way as ICCP, but when the most reactive metal is connected electrically to the steel in a corrosive environment, the difference in potentials cause it to become an anode which is consumed preferentially over the reinforcement (The Concrete Society, 2011).

2.5.3.2 Re-alkalisation

Carbonation of concrete inevitably causes a reduction in its alkalinity which in turn can result in reinforcement corrosion as discussed in Chapter 2.4.1.2. However, it is possible to restore the alkalinity of carbonated concrete, thus restoring the passive environment around the steel with minimal invasion.

This can be accomplished by passing an electrical current from an external anode through the concrete to the reinforcement. The passive alkaline environment is restored to the concrete as an alkaline electrolyte, such as sodium carbonate solution, which is initially applied to the surface, is drawn through the concrete by the current, while electrolysis at the reinforcement surface simultaneously produces a high pH environment around the steel (The Concrete Society, 2000).

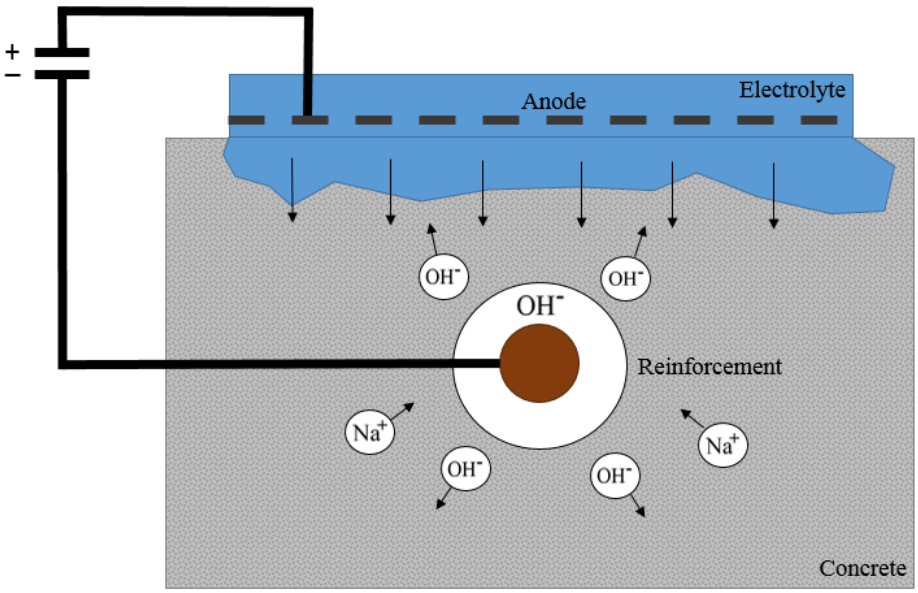

Figure 2-8 – Diagram of re-alkalisation process

2.5.3.3 Electrochemical Chloride Extraction

Electrochemical chloride extraction works in a similar manner to re-alkalisation, the difference, however, is that the aim is to remove chloride ions from the concrete and lower their level to below the corrosion threshold – the level at which corrosion will occur if water and oxygen are also available. This is achieved by applying an electrical field between an external anode mesh and the reinforcement – drawing the chloride ions towards the anode and out of the concrete, while electrolysis at the reinforcement surface simultaneously re-alkalizes the environment around the steel (The Concrete Society, 2000).

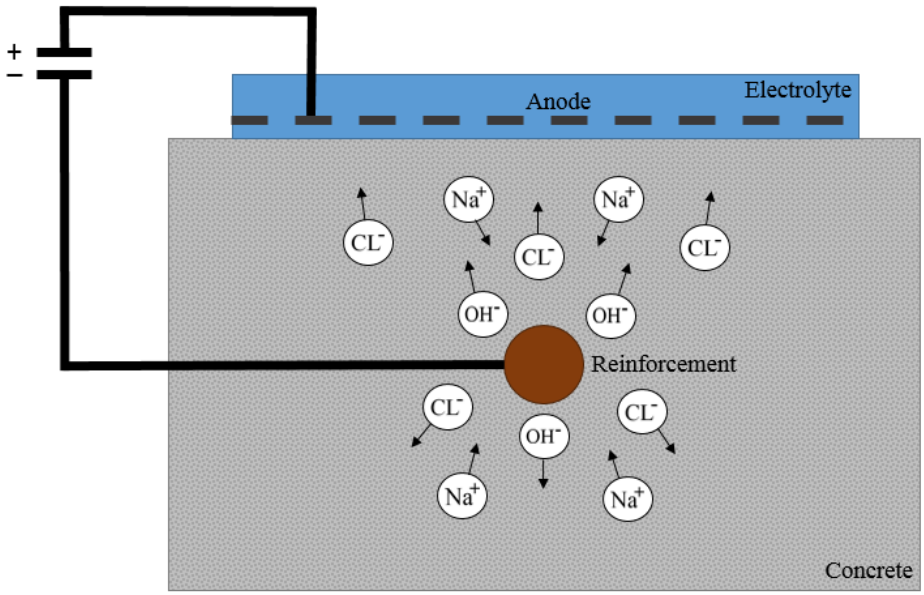

Figure 2-9 – Diagram of chloride extraction process

2.5.4 Crack Repair

It is inevitable that reinforced concrete will crack as its tensile strength is only around 10% of its compressive strength and, as a result, even relatively small tensile stresses can cause cracking. These cracks fall into one of two classes: structural cracks caused by direct loading, and intrinsic cracks resulting from chemical or physical changes within the concrete (The Concrete Society, 2015). While some cracking is expected and not generally a cause for concern, the necessity for repair is dependent on the crack width, quality of the concrete and whether the crack is active or dormant. Hairline and small dormant cracks do not require repair and may self-heal, but larger dormant cracks should be filled with a compatible material, and active cracks must be repaired by preventing further movement and filling, or by using a flexible filler that will accommodate the movement (Broomfield & Macdonald, 2003).

There is a wide range of specialist materials available for repairing cracks, including epoxies, polyesters, methacrylates, silicones, polysulphides, asphaltic materials, polymer mortars (The Concrete Society, 2015; Broomfield & Macdonald, 2003). However, as is the case with patch repairs, many of these materials may not be suitable for use in historic concrete structures.

2.5.4.1 Filling

The filling of cracks up to 0.05 mm wide is generally carried out by injection under pressure. Several small holes are drilled at regular intervals along the crack, the crack sealed at the surface with a quick-setting putty, and the repair material then applied to the through the drilled holes under pressure. Injection starts from one end and as filling progresses past each drilled hole, the hole is sealed off – continuing until the crack is completely filled. Alternatively, vertical cracks in slabs can also be filled by creating a reservoir of the repair material on the top surface and allowing gravity to force it through the crack (The Concrete Society, 2000)

2.5.4.2 Sealing

In the case of dormant cracks which are not required to perform structurally, repair can be carried out by enlarging the crack along the external face and routing, cleaning and flushing it, before applying a joint sealer which will prevent water ingress through it (Broomfield & Macdonald, 2003)

2.5.4.3 Stitching

In cases where it is necessary to re-establish the tensile strength across a crack, the concrete section can be stapled together – spreading the tension across a larger surface. However, this can result in cracking elsewhere as it results in a stiffening of the structure (Broomfield & Macdonald, 2003)

2.6 CHARACTERISTICS RELEVANT TO REPAIR

It is important to ensure that any repair materials used in concrete restoration will act in accordance with the changes of the original material, as failure to match the materials can result in a repair that is poor – both structurally and aesthetically.

2.6.1 Shrinkage of Concrete

Shrinkage occurs in concrete as it dries during and after hardening, and can lead to significant contraction of the concrete structure, which in turn can result in cracking when restrained (Kwan, *et al*., 2010). The cracking of concrete has serious implications, as it can lead to further and more severe degradation of the structure as steel reinforcement becomes exposed, and also leaves the concrete more susceptible to freeze-thaw attack.

The shrinkage properties of concrete are also an important factor for a successful repair. When attempting to repair structural concrete, it is essential that each repair situation is considered individually with a comparison of the concrete which has already completed shrinkage cycles, with the new material that will undergo shrinkage in the future (The Concrete Society, 2009a). This is important because the bond between the repair layer and the old concrete acts as an external restraint (Bissonnette, *et al*., 1999), potentially causing curling and delamination of adjacent concrete layers with different shrinkage properties (Day, 2010).

There are several factors which affect the shrinkage properties of concrete, and these include the aggregate properties, aggregate content, water content, cementitious materials, curing conditions, environmental conditions and member size and shape (Kwan, *et al*., 2010). While most of the shrinkage movement is due to the cement paste, some aggregates are also prone to shrinkage – with dense aggregate concrete generally undergoing less shrinkage than lightweight aggregate concrete (Building Research Establishment, 1991b).

2.6.1.1 Drying Shrinkage

Drying shrinkage can be defined as volumetric change due to the drying of concrete, and is related to the volume of water lost (Zhang, *et al*., 2013) from hardened concrete stored in unsaturated air (Neville & Brooks, 2010). This water is the excess from the mix which does not react with the cement, but is required to aid compaction and workability, and becomes trapped in the pores of the hardened cement paste (The Concrete Society, 2000). However, the change in volume of drying concrete is not equal to the volume of total

water removed, as free water is also lost and this causes little or no shrinkage (Neville, 2011). Typically, drying shrinkage develops much quicker near the drying surface than in the centre of a concrete element (Ayano & Wittmann, 2002), and occurs to a smaller degree in concrete than in neat cement paste as the aggregate has a restraining influence (Domone, 2001), reducing the overall concrete shrinkage by providing restraint of the cement matrix (Imamoto & Arai, 2008).

Drying shrinkage involves two different types of movement; reversible and irreversible. The irreversible movement represents a large proportion of the maximum shrinkage which occurs during the first drying period, with further wetting and drying cycles producing reversible movement (Domone, 2001). The reversible moisture movement, or wetting expansion, will typically represent between 40 and 70 percent of drying shrinkage respectively, with the effects of prolonged periods of dry weather usually reversed by a relatively short period of rain (Neville & Brooks, 2010).

Long term volumetric changes occur due to several factors, including temperature fluctuations, self-desiccation (internal drying), and loss of water from the capillary pores and the various cement hydrates (external drying) (Saliba, *et al*., 2011), which consequently cause the cement paste to contract (Neville & Brooks, 2010). This contraction is normally hindered by external or internal restraints, which induce tensile stresses that can exceed the tensile strength of the material and result in cracking (Bissonnette, *et al*., 1999). Substantial self-drying shrinkage can also occur as a result of an increase of the stress on the porous structure, which occurs when a reduction in relative humidity in the pore system causes a water-air meniscus that places considerable stress on the pore walls (Saliba, *et al*., 2011).

However, drying shrinkage is rarely a problem in modern concrete construction provided good practice is followed, with the shrinkage of the majority of concrete not exceeding 0.045% (Building Research Establishment, 1991a). To put this into perspective, the specification for precast concrete masonry units, BS 6073-1 (British Standards Institution, 1981), permits an average drying shrinkage of up to 0.06% in precast concrete masonry units, and up to 0.09% autoclaved aerated concrete blocks, while, for cast stone (homogenous and facing mixes), BS 1217 (British Standards Institution, 1986a) cites a limit of 0.04%.

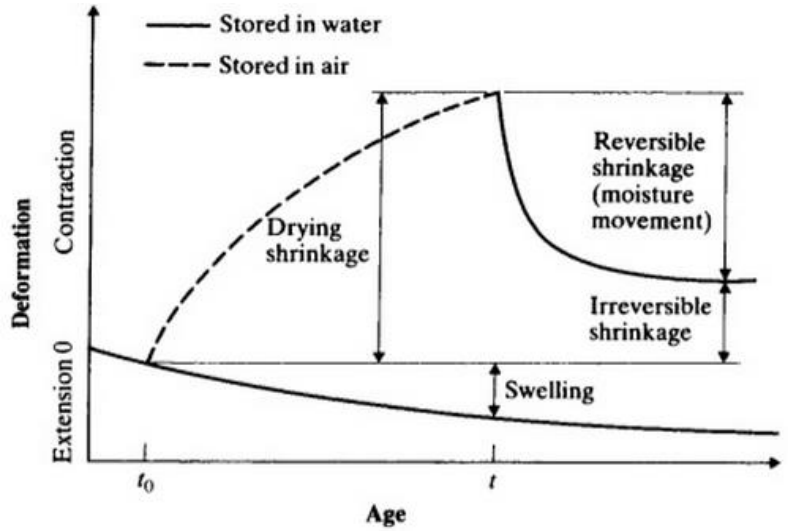

Figure 2-10 – Moisture movement in concrete which has dried from age t_0 until t and was then re-saturated, reproduced from 'Concrete Technology' (Neville & Brooks, 2010)

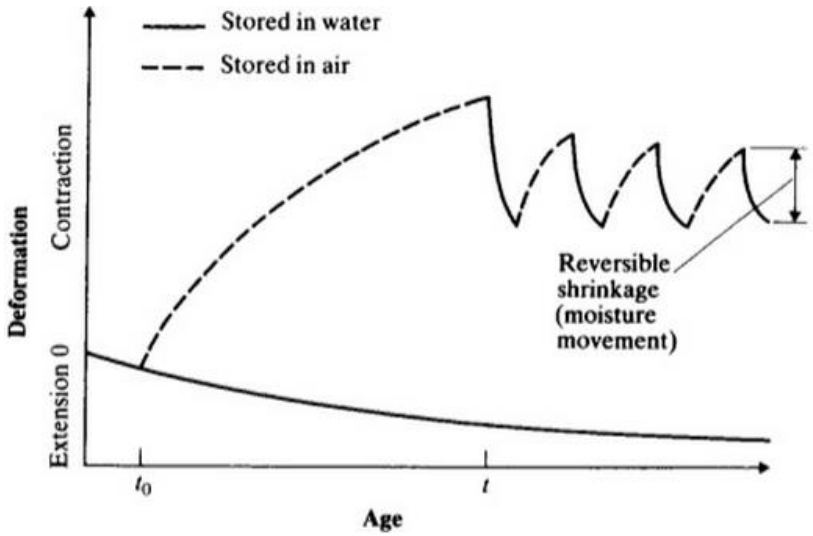

Figure 2-11 – Moisture movement in concrete which has dried from age t0 until t and was then subjected to cycles of wetting and drying, reproduced from 'Concrete Technology' (Neville & Brooks, 2010)

Influence of Cement Paste

The microstructure of a porous medium is a significant factor in its shrinkage (Imamoto & Arai, 2008), with volume changes greatly reduced by the use of low-porosity cement (Yudenfreund, *et al*., 1972). The main factors influencing the pore structure of concrete include the w/c, degree of hydration, use of supplementary cementitious materials, the presence of chemical admixtures and curing conditions, with the type of cement used and its age also having some influence (Basheer & Barbhuiya, 2010).

The influence of the w/c is twofold (Ishai, 1968). Firstly, the w/c determines the amount of evaporable water in the cement paste and the rate at which water can move to the

surface, with increasing w/c intensifying the shrinkage of the hydrated cement paste (Neville, 2011) and accelerating the other volume contraction processes (Ishai, 1968). Secondly, as there is an increase in w/c, and thus a higher percentage of capillaries and other voids within the cement matrix, it becomes less rigid and suffers a reduction in its capacity for resisting the contraction of the cement gel (Ishai, 1968).

However, at a constant w/c, increasing the cement content results in an increase in shrinkage, as there is a larger volume of hydrated cement paste with a capacity for shrinkage (Neville, 2011), with the magnitude of shrinkage in cementitious materials being directly proportional to the paste volume content (Bissonnette, *et al*., 1999).

With regards to cement fineness, Bennet & Loat (1970) found that the use of finer cement leads to a decrease in workability, which, when comparing concrete mixes of equal workability, resulted in an increase in both shrinkage and creep due to the increase of w/c required to maintain workability. In mixes of equal w/c, shrinkage and creep were only slightly increased by the use of finer cements and these increases were noted to have mostly occurred at an early age, and apparently as a result of the faster hydration associated with finer cement. However, contrary to this, Neville (2011) states that while the fineness of cement does increase the shrinkage of the neat cement paste, finer cement does not increase shrinkage of concrete, and is only a factor in so far as coarser particles, which hydrate very little, have a restraining effect similar to that of aggregate.

Influence of Aggregate

The use of aggregates reduces the shrinkage of concrete by restraining the shrinkage of the cement matrix (Imamoto & Arai, 2008). However, the selection of aggregates with appropriate shrinkage properties is essential, as the use of aggregate prone to shrinkage will result in increased shrinkage of concrete – even when good construction practice is followed (Building Research Establishment, 1991a).

The current standard, BS EN 12620 (British Standards Institution, 2008a), states that "*Where disruptive shrinkage cracking of concrete occurs due to the properties of the aggregate, the drying shrinkage associated with aggregates to be used in structural concrete shall, when required, not exceed 0.075 % when tested in accordance with EN 1367-4"*. However, prior to BS EN 12620, aggregate shrinkage was classified in BS 812-120 (British Standards Institution, 1989), which provided two categories for aggregate shrinkage, A and B, and stated the suitable uses of each class (Table 2-18).

While most natural aggregates used for concrete in the United Kingdom do not expand or shrink significantly, certain aggregates, such as those found in the industrial belt of Scotland, do exhibit high volume changes on wetting and drying, and this can cause drying shrinkage of concrete to be up to four times greater than that observed when using aggregate which is not prone to shrinkage (Building Research Establishment, 1991a). Consequently, the use of shrinkable aggregates is undesirable as it can result in serviceability issues when there is excessive deflection or warping, and can significantly impair durability if cracking occurs (Neville, 2011). In fact, the Building Research Establishment (1991a) reports that simply supported reinforced beams and slabs made with high shrinkage concrete, without imposed loading, deflect more than those made with normal shrinkage, with such deflections well in excess of the elastic deformation produced by loading.

Of the Scottish aggregates examined (Building Research Establishment, 1991a), it has been found that 60% fall into category A. These aggregates included quartz, flint gravel, limestone, marble, blast-furnace slag, granite, unaltered felsite, and a few examples of other igneous rock types such as dolerites and gabbros. However, while they did not exceed the 0.075% limit, most of these aggregates in central Scotland are at the higher end of the range of 0 to 0.075%. The other 40% of aggregates examined fell into category B. These high shrinkage aggregates are normally gravels and crushed rock consisting mainly of sedimentary rock types such as greywacke, shale and mudstone.

Table 2-18 – Categories of aggregate and recommended use, as specified in BS 812-120

CATEGORY	RANGE OF VALUES	USE
A	0 to 0.075%	All concreting purposes
B	Greater than 0.075%	Positions where complete drying out never occurs.
		Mass concrete surfaced with air entrained concrete.
		Members symmetrically and heavily reinforced not exposed to the weather

Source: BS 812-120 (British Standards Institution, 1989)

With regard to aggregate size, Zhang, *et al*. (2013) found that the effects of fine aggregates on the degree of drying shrinkage of concrete specimens were inconsiderable, and confirmed that the primary factors affecting the degree of drying shrinkage due to aggregate shrinkage are the kind of coarse aggregate, its specific surface area, absorption ratio and pore structure. The use of larger aggregates also allows the use of a concrete

mix with low cement content, also known as a 'lean mix', at a constant w/c – leading to lower shrinkage (Neville & Brooks, 2010).

2.6.1.2 Carbonation Shrinkage

Carbonation shrinkage occurs in concrete as a result of the reaction between carbon dioxide (CO_2) in the atmosphere and the hydrated paste. CO_2 forms carbonic acid in the presence of moisture, which reacts with calcium hydroxide ($Ca(OH)_2$) to form calcium carbonate ($CaCO_3$), and causes decomposition of other cement compounds (Neville & Brooks, 2010). This reaction causes both shrinkage and an increase in strength. This is because water is released as part of this reaction and, at the same time, $CaCO_3$ begins to crystallise in the pores, reducing the permeability and increasing strength (Domone, 2001).

2.6.2 Creep of Concrete

Creep of concrete is time-dependent strain that occurs under constant stress, usually externally supplied, which occurs independently of changing moisture content (Powers, 1968). In most cases, creep and shrinkage take place simultaneously, and, as with shrinkage, the porosity of the hardened cement paste also has a strong influence on creep, due to the increasing stress concentrations in the load-bearing solid skeleton as porosity increases (Wittmann, 1982). While creep and shrinkage take place simultaneously, it can be noted that creep usually has the effect of relieving the stresses induced by shrinkage before any cracking occurs (Domone, 2001).

Also – as with shrinkage – it is primarily the hydrated paste which undergoes movement, with aggregate having a restraining influence (Neville, 2011). Parrot (1970) observed four main components of creep: recoverable and irrecoverable basic creep, and recoverable and irrecoverable drying creep – with basic creep being governed by an elastic structure within the paste, and drying creep initially controlled by an oriented loss of loosely bonded hydrate paste.

In their study, Meyers & Slate (1970) concluded two things about creep. Firstly, the most important variables to affect creep were the degree of hydration at the time of loading, the amount of water present and not chemically combined at the start of loading and while the specimen is under load, and the amount of micro-cracking developed in the system before and during the time under load. Secondly, as a result of the migration of adsorbed water, not all of the creep strain is recovered over time, and this is dependent on the

volume of water adsorbed by the specimen at the time of load release and the stability of the gel and water at the time of load application and release.

With regards to the hydration process, as it continues it creates a more stable system, increasing the rigidity and strength of the solid matrix, the time-dependent processes, particularly the irreversible components, tend to decrease with hydration prior to loading (Ishai, 1968). However, when hydration occurs under a sustained load, this increase in strength and rigidity while the material is deformed results in an increase in the irreversible component of deformation (Ishai, 1968).

The w/c has a similar effect on creep as on shrinkage, with increasing w/c intensifying creep due to its role in the development of the cement matrix structure. The w/c also affects the proportion of capillary pore water available, which in turn determines the rate and amount of creep in the initial period of days after loading – an influence which is considerable in hardened cement paste, but less so in concrete and mortar (Ishai, 1968).

2.6.3 Weathering

Over time, the weathering of concrete structures is inevitable as its porous nature allows the accumulation of soiling or biological material; while this is often unsightly, it usually does not pose a significant risk to the durability of the concrete. In fact, attempts to clean the concrete surface can actually result in more serious, permanent damage (Urquhart, 2014). Consequently, historic concrete structures are usually left to weather naturally and any repair material should, over time, weather in a similar fashion so that the two materials match well visually.

However, this is problematic as the proprietary mixed repair products that are used on contemporary concrete structures usually have a higher technical performance and therefore do no provide an acceptable aesthetic match. As such, it is necessary to use specially batched concrete repair materials that will minimise the visual impact of the repair (Broomfield & Macdonald, 2003).

In order to do this though, it is important to ensure that both materials have a similar porosity and, as with shrinkage, cement content and w/c ratio are the key factors in selecting repair materials, as they are the primary influences on porosity (The Concrete Society, 2013; Neville, 2011).

3 METHODOLOGY

3.1 ASSESSMENT STRATEGY

One aim of this project is to develop a database that relates compositions of cement in concrete structures throughout Scotland to their date, architectural type, production source, and physical characteristics. However, in order to achieve this, it is necessary to carry out an in-depth assessment of the existing structure, and the materials used in its construction.

Due to the historic value and protected status of listed structures, it is not always possible to carry out the full spectrum of testing that would be required to obtain the desired characterisation of historically-significant concrete. As such, the following three-phase assessment strategy was prepared in order to maximise the output of information available from each structure and concrete sample.

- Phase 1: Desk Study
- Phase 2: Visual/Photographic Survey
- Phase 3: Material Testing

3.1.1 Desk Study

The purpose of the desk study was to establish as much information as possible about the structure and the associated construction materials prior to the removal and testing of any samples and also to fill the gaps in knowledge that cannot be obtained through material testing. In some cases, the information obtained from studying historical records, such as construction drawings and any previous test data, can be sufficient to provide an alternative to physical material testing. This contribution is particularly significant, as the protected nature of many historically-significant structures can make obtaining material samples difficult.

As many of the samples were sourced through Historic Environment Scotland, and other heritage bodies such as the National Trust for Scotland, there was, in most cases, some degree of historical information relating to the age and previous use of the structures.

Some of the samples sourced from other parties, such as the cores obtained from Scottish Water, were provided with detailed construction drawings which allowed each individual concrete specimen to be cross-referenced and dated.

3.1.2 Visual/Photographic Survey

In some cases, samples were retrieved from specific structures in Scotland. In these instances, a visual and photographic survey was undertaken of the existing structure in order to record the exact location that a sample was taken from. The importance of where the sample was taken from will be discussed in subsequent chapters.

3.1.3 Material Testing

The historic value and protected status of many of Scotland's early historic concrete structures meant that, in some cases, the degree of material available for testing was very limited. In order to maximise data output from each structure, a three-tier testing procedure was developed to deal with each level of testing that can be allowed, with non-destructive testing, testing on drilled samples, and testing on cored and mass samples being carried out.

3.1.3.1 Non-Destructive-Testing

In cases where it is was not possible to extract any samples from a structure, it had been hoped that non-destructive testing (NDT) could be carried out *in-situ*. However, NDT has significant limitations and, in most cases, can only provide information on the surface material. While this will provide limited composition data, it can help to determine the behaviour of concrete in a historic structure, which in turn can be used to establish trends in concrete from various time periods. Unfortunately, due to health and safety concerns involved with testing – such as those inherent to the use of portable X-ray equipment, the remote location of many of the structures, and the need to regularly monitor non-destructive tests – such as drying shrinkage, it was not possible to carry out any *in-situ* testing.

3.1.3.2 Drilled Samples

In some cases, drill cuttings were provided from a concrete structure. While this did not allow the same wide range of testing available on a concrete core, the provision of drilled

samples still allowed testing to determine properties such as the overall chemistry, mineralogy and cement content. The data from these tests could, in the future, be combined with *in-situ* testing, such as shrinkage monitoring, to more accurately assess the effects of composition on historic concrete performance.

3.1.3.3 Cored/Mass Samples

The provision of cored concrete samples allowed the full spectrum of tests to be carried out. Firstly, grinding solid samples provided powders which could be used in X-ray Fluorescence (XRF) analyses to determine bulk chemical compositions, and X-ray Diffraction (XRD) to determine mineralogy. Secondly, intact cores were monitored for drying shrinkage in controlled laboratory conditions and then reused for destructive tests – such as compressive strength testing and aggregate grading. Similarly, mass samples could be used for chemical and mineralogical analyses, as well as aggregate grading and drying shrinkage provided the samples were large enough.

3.2 MATERIALS

3.2.1 Historic Specimens

The protected status of many historic concrete structures has meant there was some difficulty in obtaining samples for testing and, as a result, the samples provided were in a variety of shapes, sizes and conditions. Samples were provided from a number of different agencies including Historic Environment Scotland, National Trust for Scotland and Scottish Water, as well as private owners. The inventory of samples obtained for analysis in the project can be found in Table 3-1 to Table 3-4.

As access to historic concrete was limited, the criteria for the samples included in this study was twofold: they had to have a Portland cement binder – not a lime binder – and they had to pre-date the 1950s. 1950 was selected as an arbitrary date as, in review of the literature, it was clear that by this time, the manufacture of cement and concrete was relatively well understood – with strict regulatory standards in place. However, there are two exceptions to this – sample no. 43 and 56.

While sample 43 dates to 1978 – well outside the specified age range – it is a lightweight concrete containing artificial aggregate and, as such, is an interesting case study. Furthermore, the amorphous nature of the artificial aggregate raises important questions with regards to analysis techniques – discussed in detail in Chapter 6.

Sample 56 is included as it is on the border of the cut-off date and is from a group of samples which pre-date 1950, and these provide a good comparison as they are from a fairly remote site.

It should also be noted that these tables include some lime mortar samples and one limestone sample which were provided to the project prior to any analyses which confirmed they did not contain Portland cement. While they are included in the sample list, the analyses of these samples are not included in the results and discussion section of this report as they fall outside the scope of this project.

Table 3-1 – Inventory of historic samples obtained, part 1 of 4

NO.	DESCRIPTION	AGE	TYPE	NGR	EASTING	NORTHING
01	Rosyth, Oil Storage Tank	1905	Concrete	NT 11312 82196	311312	682196
02	Sample From Underwater Site Near Roman Archelogy	-	Limestone	–	–	–
03	Arklet Dam, BH 2 At Surface	1912	Concrete	NN 35573 09335	235573	709335
04	Arklet Dam, BH 2 At 10m, Part A	1912	Concrete	NN 35573 09335	235573	709335
05	Arklet Dam, BH 2 At 10m Part B	1912	Concrete	NN 35573 09335	235573	709335
06	Arklet Dam, BH 2 At 19-20m, Part A	1911	Concrete	NN 35573 09335	235573	709335
07	Arklet Dam, BH 2 At 19-20m, Part B	1911	Concrete	NN 35573 09335	235573	709335
08	Arklet Dam, BH 4 At 1-7m	1912	Concrete	NN 35573 09335	235573	709335
09	Arklet Dam, BH 4 At 13-14m	1912	Concrete	NN 35573 09335	235573	709335
10	Loch Katrine, BH 11 At 1.92-3.47m	1856-59	Concrete	NN 44390 10128	244390	710128
11	Loch Katrine, BH 12 At 3.12-4.87m	1856-59	Concrete	NN 44390 10128	244390	710128
12	Loch Katrine, BH 13 At 2.35-3.86m	1856-59	Concrete	NN 44390 10128	244390	710128
13	Inchcolm Island, South West, Artillery Mount	1914-18	Concrete	NT 1880 8250	318800	682500
14	Inchcolm Island, South West, Artillery Mount	1914-18	Concrete	NT 1880 8250	318800	682500
15	Inchcolm Island, East, Collapsed Walls	1914-18	Concrete	NT 1880 8250	318800	682500
16	Inchcolm Island, East, Collapsed Walls	1914-18	Concrete	NT 1880 8250	318800	682500
17	Inchcolm Island, East, Collapsed Walls	1914-18	Concrete	NT 1880 8250	318800	682500
18	Inchcolm Island, East, Collapsed Walls	1914-18	Concrete	NT 1880 8250	318800	682500
19	Inchcolm Island, Quarters	1914-18	Render	NT 1880 8250	318800	682500
20	Talla Aqueduct	1901-05	Concrete	NT 10648 23099	310648	623099
21	Tarlair, Open Air Swimming Pool	1930-31	Concrete	NJ 71982 64661	371982	864661

Table 3-2 – Inventory of historic samples obtained, part 2 of 4

NO.	DESCRIPTION	AGE	TYPE	NGR	EASTING	NORTHING
22	Souden Kirk, Repair	1910-11	Mortar	NT 63141 09164	363141	609164
23	Souden Kirk, Repair	1910-11	Mortar	NT 63141 09164	363141	609164
24	East Fortune Airfield, Building 47		Render	NT 55565 78959	355565	678959
25	East Fortune Airfield, Building 31		Render	NT 55565 78959	355565	678959
26	East Fortune Airfield, Air Raid Shelter		Render	NT 55565 78959	355565	678959
27	Unst, Halligarth, Front Building	1830	Mortar Powder	–	–	–
28	Unst, Halligarth, Rear Building	1839	Mortar Powder	–	–	–
29	Tentsmuir Forest, Tank Trap	1940-41	Concrete	NO 50540 27300	350540	727300
30	Tentsmuir Forest, Tank Trap	1940-41	Concrete	NO 50540 27300	350540	727300
31	Tentsmuir Forest, Cookhouse, Interior Lintel	1940-41	Render	NO 4817 2385	348170	723850
32	Tentsmuir Forest, Cookhouse, Interior Wall	1940-41	Render	NO 4817 2385	348170	723850
33	Tentsmuir Forest, Cookhouse, Roof	1940-41	Render	NO 4817 2385	348170	723850
34	Tentsmuir Forest, Concrete Plinth	1940-41	Concrete	NO 4817 2385	348170	723850
35	Tentsmuir Forest, Bombing Run Observation Tower,	1940-41	Render	NO 50400 26200	350400	726200
36	Tentsmuir Forest, Bombing Run Observation Tower,	1940-41	Foamed Concrete	NO 50400 26200	350400	726200
37	Tentsmuir Forest, Observation Tower	1940-41	Concrete	NO 50330 25800	350330	725800
38	Tentsmuir Forest, Decoy Airstrip Bunker	1940-41	Render	NO 49360 22150	349360	722150
39	Tentsmuir Forest, Collapsed Observation Platform	1940-41	Render	NO 4817 2385	348170	723850
40	Tentsmuir Forest, Collapsed Observation Platform	1940-41	Render	NO 4817 2385	348170	723850
41	Tentsmuir Forest, Collapsed Observation Platform	1940-41	Render	NO 4817 2385	348170	723850
42	Chesterhill, WWII Lookout	-	-	–	–	–

Table 3-3 – Inventory of historic samples obtained, part 3 of 4

NO.	DESCRIPTION	AGE	TYPE	NGR	EASTING	NORTHING
43	Friarton Bridge	1978	Lightweight Concrete	NO 13074 21652	313074	721652
44	Carden Bridge, Honeycombed Core 1	1936	Concrete	NJ 6931 2571	369310	825710
45	Carden Bridge, Honeycombed Core 2	1936	Concrete	NJ 6931 2571	369310	825710
46	St. David's North Church, Precast Concrete Block 1	1929	Precast Concrete	NO 39034 31844	339034	731844
47	St. David's North Church, Precast Concrete Block 2	1929	Precast Concrete	NO 39034 31844	339034	731844
48	St. David's North Church, Concrete From Foundations.	1929	Concrete	NO 39034 31844	339034	731844
49	Liberton Gardens, Outlet House 2, Wall Infill	1880	Concrete	NT 27384 69340	327384	669340
50	10 Carse View, Bearsden	1937-39	Render	NS 55228 72894	255228	672894
51	Glasgow School Of Art, Pallet A/1	1908-09	Mortar	NS 58435 65970	258435	665970
52	Glasgow School Of Art, Pallet A/2	1908-09	Mortar	NS 58435 65970	258435	665970
53	Glasgow School Of Art, Pallet E4	1908-09	Lime Mortar	NS 58435 65970	258435	665970
54	Glasgow School Of Art, Pallet E16	1908-09	Lime Mortar	NS 58435 65970	258435	665970
55	Glasgow School Of Art, Pallet P15	1908-09	Lime Mortar	NS 58435 65970	258435	665970
56	Bunavoneadar, Whale Oil Tank	1950-53	Concrete	NB 1310 0397	113100	903970
57	Bunavoneadar, Hardstanding	1923-28	Concrete	NB 1310 0397	113100	903970
58	Bunavoneadar, Hardstanding	1923-28	Concrete	NB 1310 0397	113100	903970
59	Bunavoneadar, Flensing Area	1923-28	Concrete	NB 1310 0397	113100	903970
60	Bunavoneadar, Laboratory Wall	1923-28	Concrete	NB 1310 0397	113100	903970
61	Bunavoneadar, Laboratory Wall	1923-28	Render	NB 1310 0397	113100	903970
62	Upper Kenly Farm, WWII Structures	1939-45	Render	NO 571 124	357100	712400
63	Upper Kenly Farm, WWII Structures	1939-45	Render	NO 571 124	357100	712400

Table 3-4 – Inventory of historic samples obtained, part 4 of 4

NO.	DESCRIPTION	AGE	TYPE	NGR	EASTING	NORTHING
64	Upper Kenly Farm, WWII Structures	1939-45	Render	NO 571 124	357100	712400
65	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
66	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
67	Upper Kenly Farm, WWII Structures	1939-45	Render	NO 571 124	357100	712400
68	Upper Kenly Farm, WWII Structures	1939-45	Render	NO 571 124	357100	712400
69	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
70	Upper Kenly Farm, WWII Structures	1939-45	Render	NO 571 124	357100	712400
71	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
72	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
73	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
74	Upper Kenly Farm, WWII Structures	1939-45	Concrete	NO 571 124	357100	712400
75	Upper Kenly Farm, Old Rail Bridge	-	-	NO 571 124	357100	712400
76	Flotta, Buchanan Battery	1940-42	Concrete	ND 37443 93368	337443	993368
77	Flotta, Buchanan Battery	1940-42	Concrete	ND 37468 93536	337468	993536
78	Flotta, Buchanan Battery	1940-42	Concrete	ND 37512 93350	337512	993350
79	Flotta, Golta WWII, Z Battery	1940-42	Concrete	ND 36880 95614	336880	995614
80	Flotta, Underground Bunker, Roan Head	1940-42	Concrete	ND 38610 95792	338610	995792
81	St Barevans Church, Mortar From Interior Wall	-	-	–	–	–
82	Maryculter House, Church & Burial Ground,	-	-	–	–	–
83	Kirkton Of Leochel, St Marnoch's Church & Churchyard	-	-	–	–	–
84	Bowling Swing Bridge, Core - Part A	1896	Concrete	NS 45119 73550	245119	673550
85	Bowling Swing Bridge, Core - Part B	1896	Concrete	NS 45119 73550	245119	673550

It is clear from the sample inventory that there were significantly more samples provided from the first half of the 20th century than the 19th century despite Portland cement's initial patent dating back to 1824. Furthermore, many of the samples provided date back to the First or Second World War and originate from defensive structures.

This is perhaps indicative of three things: Firstly, that the use of Portland cement in concrete, mortar and render was becoming increasingly more common in the first half of the 20th century. Secondly, that Portland cement was seen to be a suitable material from which strong and durable structures that could be built with relative haste, and, finally, that many structures that date back to the first half of the 20th century – such as war defences – have not yet been scheduled and therefore are easier to access for sample removal.

3.2.2 Preparation of Control Study Specimens

3.2.2.1 Portland Cement

Hanson CEM I 42.5N (Portland cement of strength class 42.5N) conforming to BS EN 197-1 (British Standards Institution, 2011) was used exclusively in the preparation of concrete tests specimens.

3.2.2.2 Aggregates

Three different grades of locally sourced aggregates were used for the duration of this study, two of which were coarse aggregate and one of which was fine aggregate. The course aggregates used were natural local gravels of sizes 4 - 10 mm and 10 - 20 mm, and the fine aggregate was natural local sand – all conforming to BS EN 12620 (British Standards Institution, 2008a). All aggregates were air-dried in the laboratory before use.

3.2.2.3 Water

Potable mains tap water, as specified in BS EN 1008 (British Standards Institution, 2002), was used for all mixing and curing of test specimens used in this study, except where stated otherwise. Water that had been deionised and distilled was used in testing where required by the relevant standards in order to achieve specific objectives.

3.2.2.4 Concrete Mixing Procedure

All concrete was mixed in a 0.035m^3 horizontal pan mixer in accordance to BS 1881-125 (British Standards Institution, 2013a). The sequence of concrete mixing was as follows:

1. The mixer pan and paddles were lightly dampened.
2. All aggregates were added to the mixer in the order: approximately 50% coarse aggregate, fine aggregate, sand, remaining coarse aggregate.
3. The aggregate was spread evenly over the pan, the lid of the mixer closed and the aggregates mixed for 30 seconds.
4. Half the mixing water was added and mixing was continued for 2-3 minutes.
5. The lid of the mixer was then raised and the specimen was mixed thoroughly by hand in order to ensure homogeneity.
6. The lid of the mixer was closed and the material left for 8 minutes in order to allow water absorption by the aggregates.
7. The cement was then spread over the aggregates and mixed for 30 seconds.
8. The mixer lid was raised and the paddles cleaned by hand. The concrete mixture was again thoroughly mixed by hand in order to ensure homogeneity.
9. Mixing was immediately recommenced and the remaining water added to the mixture over 30 seconds. Mixing then continued for a further 2 minutes.
10. The mixer was stopped and the concrete mixed thoroughly by hand one final time.

3.2.2.5 Casting and Curing Procedure

The concrete was then cast in moulds conforming to BS EN 12390-1 (British Standards Institution, 2012a). Prisms of dimensions 500x100x100 mm were cast and later sawn into sections for use in the Control Study, and standard cubes of dimensions 100x100x100 mm were cast for compression tests.

All moulds were prepared prior to mixing and coated with a thin layer of oil-based lubricant. Immediately after casting all moulds were stored in the laboratory under wet hessian sheets for 24 ± 2 hours. After this time, they were transferred to tanks where they were cured in water at 20°C until they reached an age of 28 days, at which time testing began immediately.

3.3 TEST METHODOLOGIES

3.3.1 Density of Hardened Concrete

The density of each hardened concrete sample was determined in accordance with BS EN 12390-7:2009 (British Standards Institution, 2009a), and weighed in the 'as-received', 'oven-dried' and 'fully saturated' states. The mass of the as-received specimens, m_r, was recorded. The specimens were then cured in water for 72 hours to allow them to become fully saturated, and the saturated mass, m_s, measured. While still saturated to constant mass, each specimen was placed on a stirrup, immersed in water and weighed, to allow the volume to be calculated, as instructed in the standard, using the formula:

$$V = \frac{m_a - [(m_{st} + m_w) - m_{st}]}{\rho_w} \quad (17)$$

where:

V is the volume of the specimen in m^3;
m_a is the mass of the specimen in air, in kg;
m_{st} is the apparent mass of the immersed stirrup, in kg;
m_w is the apparent mass of the immersed specimen, in kg;
ρ_w is the density of water, at 20°C, taken as 998 kg/m^3.

The density can then be calculated using the formula:

$$D = \frac{m}{V} \quad (18)$$

where:

m is the mass of the specimen;
V is the volume of the specimen, as calculated above.

3.3.2 Aggregate Content

The aggregate content was calculated in accordance with the BS 1881-124 (British Standards Institution, 2015a) method for calculating insoluble residue. However, as no reference samples of aggregate were available, it was assumed that none of the aggregates were acid-digestible.

A sample of each concrete was broken up using hand tools and then ground in a ball mill to produce a fine powder which passed through a 125μm sieve. A 5g sub-sample of the

powder was placed in a beaker and 100ml of 10% hydrochloric acid solution added. These were then stirred with a magnetic stirrer for 20 minutes at room temperature. Once it had been allowed to settle, the liquid was then filtered through a filter paper supported on a perforated cone. The residue was washed in the beaker with three 25ml portions of the dilute hydrochloric acid and passed through the original filter paper. The filter paper and any contained residue were then placed back in the beaker, 100ml of sodium carbonate solution (50g/L) added and placed on boiling water bath for 15 minutes. The full contents of the beaker were then filtered through a filter paper on a perforated cone, washed six times with an ammonium chloride solution (1g/L), twice with 10% hydrochloric acid solution, and then twice with warm, distilled water. The filter paper was dried at 105 ± 5°c for 24 hours, allowed to cool, and then weighed – with the mass of the filter paper subtracted to give the mass of the residue. The aggregate content of the analytical sample was then calculated to the nearest 0.1% from the equation:

$$Aggregate\ content = \frac{mass\ of\ insoluble\ residue}{mass\ of\ analytical\ sample} \times 100 \qquad (19)$$

3.3.3 Loss-on-ignition (LOI)

Between 1g and 2g of powdered sub-sample was placed in a previously ignited and weighed crucible. The crucible was then placed in a furnace and the temperature slowly raised to 1000 ± 25°C, and held at this temperature for 30 minutes, after which the sample was allowed to cool to room temperature in the furnace before being removed and weighed. Loss on ignition was calculated to the nearest 0.1% using the following equation:

$$LOI = \frac{mass\ of\ analytical - mass\ of\ ignited\ sample}{mass\ of\ analytical\ sample} \times 100 \qquad (20)$$

3.3.4 Bulk Chemical Composition (XRF)

X-ray fluorescence (XRF) spectrometry is a technique used to quantify the chemical composition of specimens by measuring the intensities of the X-ray spectral lines that are emitted by secondary excitation. When the primary beam from an X-ray tube irradiates a specimen it excites each chemical element, causing it to emit secondary spectral lines which have wavelengths characteristic to that element. The intensities of these wavelengths are measured by a detector and, as these are indicative of the concentration of the element, the bulk chemical composition can be calculated (Lawrence, 1998).

A PANalytical Zetium X-ray Fluorescence Spectrometer (XRF) with RhKα radiation source was used to determine the bulk oxide composition of powdered materials compacted into 32 mm diameter pellet moulds. The pellets were compacted at 50 kN for a minimum of 1 minute and then at 100 kN for a minimum of 4 minutes before being placed inside the XRF device and analysed. In some analyses, particularly that of quartz-rich aggregate powder, it was necessary to add to an X-ray transparent oil polymer to provide adequate cohesion within the compacted pellets.

3.3.5 Mineralogy (XRD)

A Siemens D5000 X-ray Diffractometer (XRD) with monochromatic CuKα radiation source and curved graphite, single crystal chronometer (30 mA, 40 kV) was used to analyse the mineralogical composition of powdered concrete and aggregate samples.

When a crystalline specimen is exposed to X-rays of a particular wavelength, the X-rays are diffracted by the layers of atoms in each crystalline phase – producing a characteristic pattern of peaks (Mehta & Monteiro, 2006), as shown in Figure 3-1.

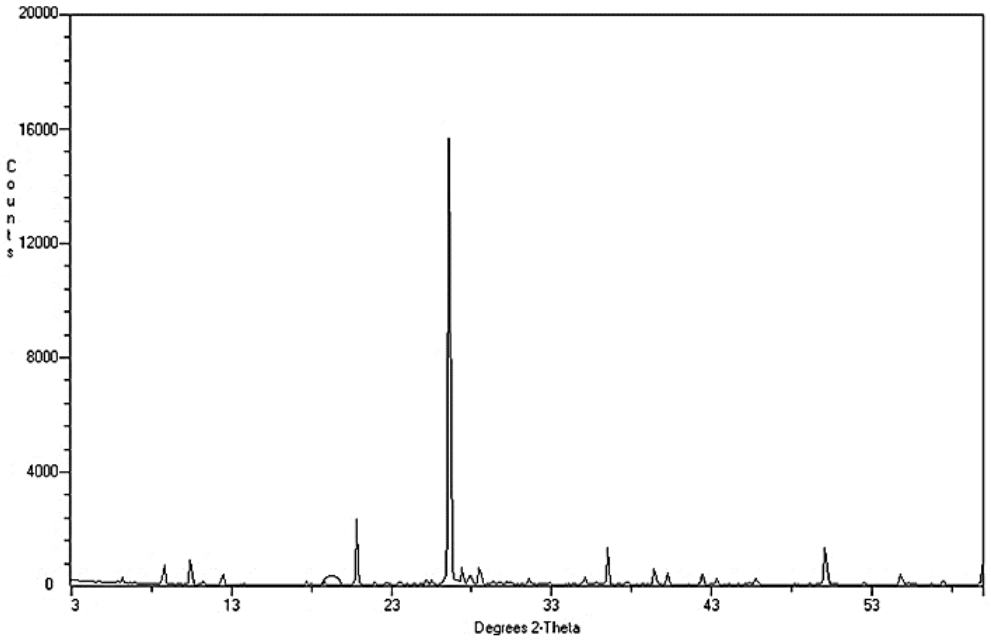

Figure 3-1 – Peak pattern from XRD of a concrete sample

From this plot, it is possible to identify the individual mineral phases present in the specimen based on their characteristic peaks at particular diffraction angles on the x-axis and quantify their proportional amount from the intensity of the peak height on the y-axis using the Rietveld refinement method.

However, the presence of amorphous phases in a specimen complicates the quantification of the crystalline phases as the amorphous phases are not detected by XRD, and so the

calculated phase quantities are only correct in relation to the sum of all the crystalline phases. As such, crystalline Al_2O_3 (corundum) was added to the test specimens at 5% total weight of the test specimen as an internal standard to aid the quantification of the crystalline components during the Rietveld refinement. Each powdered test specimen was then uniformly compacted into a test cell, with care taken to minimise preferential alignment of particles.

Figure 3-2 – Siemens D5000 XRD (left) and PANalytical Zetium XRF (right)

3.3.6 Drying Shrinkage

Drying shrinkage strain was monitored on solid concrete samples following the recommendations for mechanical measurement found in BS 1881-206 (British Standards Institution, 1986b). Two DEMEC studs were secured with a two-part epoxy resin, 4 inches apart, on one face of solid concrete samples. In the case of concrete cores, sets of two studs were secured across three axes.

After the resin had set, the solid concrete specimens were placed in water for 72 hours, to allow them to become fully saturated. These were then removed and the mass and distance between the DEMEC studs recorded. The samples were stored in an environmental chamber – which controlled relative humidity (50-60%) and temperature (21±1°C) – and were monitored for 85 days – with the mass, distance between DEMEC points and environmental conditions recorded. After 85 days the samples were placed in an oven and dried for 5 days at 105°C, after which they were allowed to cool to room temperature before measuring the mass and distance between DEMEC points.

The distance between DEMEC studs was measured mechanically using a lever linkage with the movement magnified by a sensitive dial gauge, which calibrated using an invar steel reference bar. The strain was then calculated by multiplying the difference between

the saturated and daily readings by the strain represented by each division of the dial gauge (1.99×10^{-5}).

Figure 3-3 – Concrete core with DEMEC studs (left) and strain gauge (right)

3.3.7 Particle Size Distribution (Dry Sieving)

Aggregate was removed from the bulk concrete specimens in accordance with BS 1881-124 (British Standards Institution, 2015a). A sample of each solid concrete specimen was heated in a furnace to 400 ± 5°C for up to 16 hours to assist in breaking up the binder without damaging the aggregate. The sample was then manually broken up – with care taken not to damage the aggregate, and the binder dissolved in a 10% hydrochloric acid solution of appropriate volume, at approximately 50°C. The remaining liquid was filtered through a filter paper on a perforated cone and the remaining aggregates were washed three times, with each washing having a volume of 100-200mL. The residue was then returned to the beaker with 100mL of water, before adding 100mL of sodium carbonate solution (50g/L) and simmering gently for 15 minutes. The remaining material was then washed six times with an ammonium chloride solution (1g/L), twice with 10% hydrochloric acid, and twice with warm, distilled water. The remaining aggregate was dried at 105 ± 5°C for 24 hours, allowed to cool, and then weighed.

The grading of the aggregate was then measured following the dry sieving procedure described in BS EN 933-1 (British Standards Institution, 2012b) and using standard sieves conforming to BS EN 933-2 (British Standards Institution, 1996b). The specimen material was placed in the sieving column, with the sieves arranged in order of decreasing aperture opening size and the column manually shaken. Sieves were removed one by one and shaken individually, using a pan and lid to ensure no material was lost. The passing material was then transferred into the next sieve size and process repeated. The mass of

each sieve was then weighed and the mass of the empty sieve subtracted from this in order to calculate the mass of sample retained.

3.3.7.1 Fineness Modulus

In order to include the results of the sieve analyses in later factor analysis, each aggregate grading was defined in terms of a single factor, known as the 'fineness modulus.' The fineness modulus (FM) is defined as the sum of the cumulative percentages *retained* on the sieves of the standard series divided by 100; with increasing FM values representing coarser grading (Neville & Brooks, 2010).

3.3.8 Mercury Intrusion Porosimetry (MIP)

Mercury intrusion porosimetry (MIP) was used to gain a better understanding of the pore network – in particular the larger capillary pores, which have an important influence on permeability and shrinkage (Mindness & Young, 1981). It was carried on either an 8 mm diameter core or several small lumps of a sample which had been manually broken down to fit inside the testing cell, that had been vacuum dried at 40°C for 24 hours.

MIP works on the basis that liquids which do not wet a porous solid can only enter its pores under pressure. In this case, mercury, which does not wet the paste surface due to its high surface tension, was forced into the pores of the hardened material by an externally applied pressure in two stages; firstly in a low-pressure system, and then in a high-pressure system. In both cases, the pressure is raised progressively and volume of mercury that penetrates the porous sample recorded as a function of pressure – providing what is known as a 'porogram', which must then be normalised by dividing the intruded volume by the specimen mass to give a value in m^3/g (Aligizaki, 2006).

If it is assumed the pores are cylindrical, the pressure, p, required to force mercury into the pores can be determined by the Washburn equation (Taylor, 1997):

$$p = -4\gamma cos\theta / d \tag{21}$$

However, as the applied pressure is known in this case, this equation can be rearranged to calculate relative pore diameters:

$$d = -4\gamma cos\theta / p \tag{22}$$

where:

γ is the surface energy of the liquid;

θ is the contact angle;

d is the pore diameter.

However, despite the fact that MIP is widely used in the study of cement pastes, there is some doubt over the accuracy of this technique. Taylor (1997) raised the following five concerns:

1. This technique measures pore-entry sizes, not the distribution of pore sizes, and so if large pores can only be accessed through narrow entrances they will be incorrectly registered as smaller pores.
2. The delicate pore structure of the paste is altered by the high stress needed to intrude mercury.
3. Prior to testing the sample must be intensively dried, which results in an alteration of the pore structure as water is removed.
4. It is unclear to what extent this technique registers the coarsest part of the porosity, intruded at low applied pressures.
5. The calculations involved assume both cylindrical pores and a particular contact angle – either of which may be incorrect.

It should be noted that in this study analyses were carried out on samples containing both fine and coarse aggregates, which will have a significant effect on the results obtained, as aggregate generally has a much lower porosity than neat cement paste. Furthermore, there is a difference in porosity between concrete and neat cement paste at the same w/c due to the presence of larger pores that do not exist in neat cement paste, and this variation increases as hydration progresses (Neville, 2011). As such, the porosity results obtained from MIP should only be considered representative of the material as a whole, and not of the cement paste only, and in any comparison of results the aggregate content and type of each sample must be taken into consideration as a significant factor.

3.3.9 Nitrogen BET Adsorption

While MIP gives a greater appreciation of the larger capillary pores, gas adsorption is useful for gaining a more thorough understanding of the small capillaries and micropores that make up the gel porosity (Mindness & Young, 1981). As with MIP, this procedure was carried on either an 8 mm diameter core or several small lumps of a sample which had been manually broken down to fit inside the testing cell. The samples were subjected to an outgassing procedure within the apparatus – removing any previously adsorbed gases, then exposed to N_2 at 77K and the adsorption measured. While water vapour can

be used as the adsorbate for Brunauer-Emmett-Teller (BET) analysis, nitrogen is normally preferred when dealing with hydrous oxides as it less chemically sensitive (Bye, 1999).

This technique is based on the principle that when a porous solid (adsorbent) is exposed to gas of a particular volume (adsorbate) under a finite pressure, it begins to adsorb the gas molecules on its outside surface and inside pores, which is accompanied by an increase in the mass of the solid and a decrease in the pressure of the gas (Aligizaki, 2006). From the results obtained from the N_2 adsorption test it is possible to calculate the specific surface area of the sample using equation (23), where S is the specific surface area in m^2/g, and V_m is calculated using the BET equation (24) (Aligizaki, 2006):

$$S = 4.35 V_m \times 10^6 \quad (23)$$

Where:

- 4.35 is the area (m^2/g) occupied by 1 cm^3 of nitrogen
- V_m is the volume of nitrogen per gramme of adsorbent (m^3/g) required for a complete monomolecular surface layer

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (24)$$

Where:

- P is the pressure (N/m^2)
- P_0 is the saturation pressure (N/m^2)
- C is the BET constant, function of the net heat of adsorption
- V is the volume of nitrogen (m^3 per gramme of adsorbent) at pressure P

However, there are two complications associated with this technique (Bye, 1999):

1. There is no clear distinction between the removal of adsorbed and chemically bound water which occurs during the degassing procedure.
2. The value obtained for the surface area is dependent on the adsorbate used.

Furthermore, in the overlapping range of pore sizes, the data obtained from MIP and adsorption experiments may not agree very well (Mindness & Young, 1981), as can be seen in Figure 3-4:

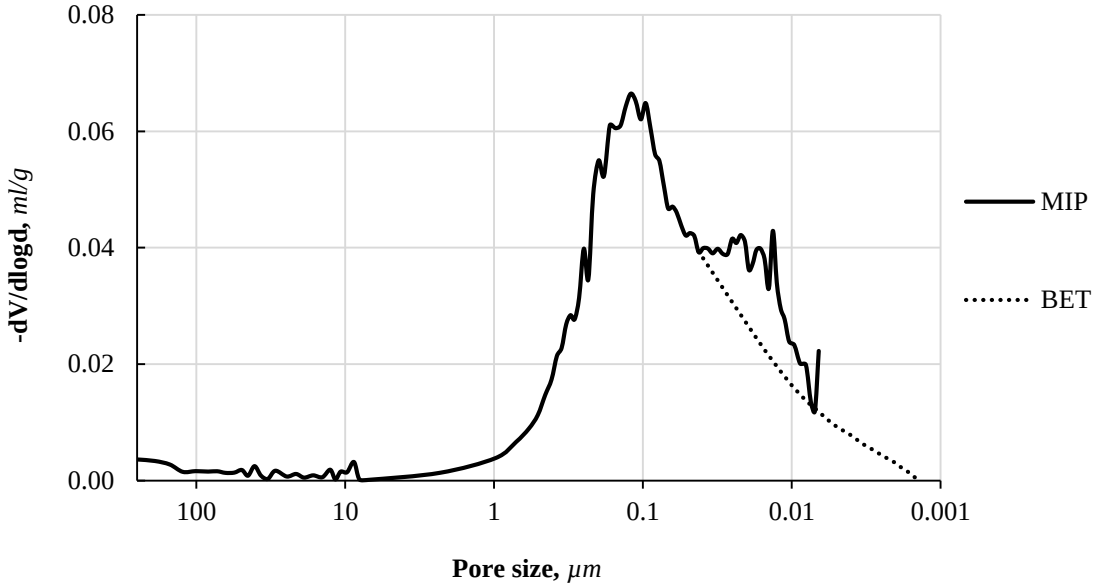

Figure 3-4 – Comparison of results from MIP and nitrogen BET adsorption tests

3.3.10 Statistical Analysis

A key component in the successful repair of concrete structures is understanding and matching the physical properties of the specific material that is to be repaired. As previously discussed, the chemical and physical composition of an individual concrete sample significantly affect these properties.

One of the aims of this project was better understand which specific aspects of chemical and physical composition have the greatest effect on the relevant physical properties that need to be matched by a repair material. By determining which factors are the most crucial in determining the physical properties of the material, it will be possible for those carrying out a repair to more successfully manipulate the composition of the repair material, in order to match the required physical properties. However, this is complicated by a large number of variables. As such, statistical analysis software Minitab 13 was used to help establish the weighting of each variable.

3.3.10.1 Best Subset Regression

Best subset regression is an automated procedure in Minitab, which was used to help identify the most crucial variables affecting ultimate drying shrinkage. In this procedure, a set of variables which – based on the review of literature – seemed most likely to influence drying shrinkage, were fed into the program which then created regression models containing subsets of variables. The outputs from Minitab – 'R^2', 'R^2 *adjusted*', '*Mallows' Cp*', and '*S*' – were then used to identify the best-fitting regression model and,

therefore, the variables most likely to influence ultimate drying shrinkage. However, in order to assess the models, it is first necessary to understand the function of the outputs.

R^2, also known as the coefficient of determination, is the percentage of response variable variation that is explained by its relationship with one or more predictor variables. The value of R^2 is always between 0-100 percent, with higher values usually indicating better fit of the model to the data (Minitab, 2016).

R^2 adjusted is the coefficient of determination adjusted for the number of variables in the model, to take into consideration that the addition of terms to a subset model will always result in an increase in the R^2 of that model (Minitab, 2016). As such, R^2 adjusted is used when comparing subset models containing different numbers of variable terms.

Mallows' Cp is also used to compare subset models containing different numbers of variable terms – but functions by comparing the precision and bias of the full model to that of the subset models – and is an indication of the precision of the model (Minitab, 2016). The closer the Mallows' Cp is to the number of parameters in the model, the more precise the model is – with values increasingly greater than the number of parameters indicating increasing bias and lack-of-fit.

S is the standard error of the regression – measured in the units of the response variable – and represents the standard distance that data values fall from the fitted regression line. Low values of S represent a more accurate response from the subset model, and, therefore, is used to compare the accuracy of different models (Minitab, 2016).

3.3.10.2 Multivariate Analysis

The multivariate analysis considers several related 'random' variables simultaneously, with each one considered equally important at the start of the analysis (Manly, 1986). The analysis then simplifies the data, summarising the large body of data in terms of relatively few parameters (Chatfield & Collins, 1980). There are several multivariate analysis methods that can be employed, but this project will primarily use 'best subset regression' and 'factor analysis.

Factor Analysis

Factor analysis attempts to account for the variation in a number of original variables using a smaller number of index variables, known as 'factors' and assumes that each of the original variables can be expressed as a linear combination of these factors, (Manly,

1986). Variances which are unexplained by the common factors are then described by the addition of a residual 'error' term (Chatfield & Collins, 1980).

These factors have a loading between -1 and 1, which indicates how strongly that particular factor affects the variable. The closer the loading is to -1 or 1, the stronger the effect of the factor – with loadings closer to zero, indicating a weaker effect (Minitab, 2016).

The loading pattern of the factors can be adjusted by orthogonal rotation of the axes. This can make the loading patterns easier to interpret by simplifying either the columns or rows of the matrix. Three different types of rotation are detailed in Table 3-5.

Table 3-5 – Methods of orthogonal rotation

ROTATION	GOAL
Equimax	To rotate the loadings so that a variable loads high on one factor but low on others.
Varimax	To maximizes the squared factor loadings in each factor. That is, to simplify the columns of the factor loading matrix. In each factor the large loadings are increased and the small ones are decreased so that each factor only has a few variables with large loadings.
Quartimax	To maximize the variance of the squared factor loadings in each variable. That is, to simplify the rows of the factor loading matrix. In each variable the large loadings are increased and the small ones are decreased so that each variable will only load on a few factors.

Source: Minitab (2016)

4 CONTROL STUDY

4.1 INTRODUCTION

Given the significant role the original mix proportions and w/c ratio play in the porosity and subsequent physical characteristics of concrete, it is, understandably, desirable to replicate these in a repair material. Unfortunately, current standards for determining mix proportions and w/c ratio, such as BS 1881-124 (British Standards Institution, 2015a) and NT Build 361 (Nordtest Method, 1999), are not suitable for use with historic concrete. However, despite their lack of suitability, the current standards are regularly applied in the assessment of historic structures as there are simply no alternatives. This presents a problem as the potential inaccuracy of the standard test methods is not included in test reports, and these may have a significant impact on the repair strategy applied to historic concrete structures.

4.2 SCOPE OF THE PROBLEM

BS 1881-124 determines w/c ratio indirectly, through separate determinations of cement content and water content. However, The Concrete Society (The Concrete Society, 2014) determined that, in favourable circumstance and with reliable analysts, the w/c ratio could only be calculated to within ± 0.1. In order to even achieve this low level of accuracy, a petrographical examination of the concrete is first required to determine whether acid soluble aggregate is present, as the standard utilises acid digestion of the cement matrix to determine the cement content. Furthermore, the standard itself claims that 'acceptable' results are only possible when the concrete is less than five years old and without physical or chemical damage. Consequently, the degree of accuracy of this method would be even lower for aged and carbonated concrete samples, rendering it insufficient for an accurate analysis of historic structures.

NT Build 361 describes a method of estimating w/c ratio in hardened concrete, using microscopic investigation of thin sections impregnated with a fluorescent agent. These thin sections are then compared to a series of laboratory prepared reference samples and the w/c ratio determined by comparing the fluorescent intensity of the samples. However, the accuracy of this method has also been called into question with some authors (St John, 1994; Neville, 2003) claiming a realistic accuracy of ± 0.1 for w/c ratio within the range of 0.4 to 0.6. Moreover, the necessity for reference samples and the reduction in pore volume due to carbonation make this method also unsuitable for historic concrete. While work has been undertaken in developing new methods of determining w/c ratio, such as that by Wong & Buenfeld (Wong & Buenfeld, 2009), there is, at present, no adequate or standardised method for accurately determining the w/c ratio of historic concrete.

Furthermore, there is a significant challenge facing those tasked with performing analysis on historic concrete structures. The challenge is twofold: firstly, when dealing with historic structures it often difficult to obtain the volume of samples required to carry out analysis, and secondly, the samples that can be obtained are not necessarily representative of the area requiring repair, or even of the concrete in general. This issue is particularly problematic when dealing with historic structures, as owners are, understandably, reluctant to allow further damage to occur to a structure in order for samples to be taken, and is exacerbated when dealing with listed structures or scheduled monuments as, in the United Kingdom, it is a criminal offence to remove material without written consent from the Secretary of State (Department for Culture, Media & Sport, 1979).

To put this issue in perspective, BS 1881-124 (British Standards Institution, 2015a) requires a minimum of two representative samples to be taken for analysis of hardened concrete from a source of less than 6 m^3 and a minimum of ten independent samples from larger volumes of concrete. Furthermore, the mass should not be less than 1 kg in any case, not less than 2 kg to determine original water content, and not less than 4 kg if aggregate grading is to be determined. To even carry out a qualitative petrographical analysis of hardened concrete, for which there currently exists no British or European Standard, ASTM C 856 requires a minimum sample size of at least one core, preferably 6 in. (152 mm) in diameter and 1 ft. (305 mm) long for each mixture or condition or category of concrete (ASTM International, 2004). As such, it is understandably difficult to obtain permission to remove the minimum mass of material that would be required for a thorough analysis of a historic concrete structure.

This lack of available material can often result in analysts being asked to carry out investigations on samples which are smaller in relation to a standard's requirement for a representative sample – whether that is a mass sample for physical/chemical analysis or a thin section for microscopical analysis. These samples are also often supplied with little information as to where exactly on the structure they were taken from, preventing the analyst from being able to provide a context for their results; a necessity when dealing with a material as heterogeneous as concrete.

4.3 METHODOLOGY

In order to fully assess the limitations of the current standards when used in the analysis of historic concrete samples, nine concrete mixes were produced using Portland cement (CEM I 42.5N) as the sole cement constituent, and with mix proportions (Table 4-1) based on typical mix designs from the early 20th century (Somerville, 2001; The Concrete Society, 2009b; Yeomans, 1997; Abrams, 1922). These proportions were approximately 1:1:2, 1:2:4 and 1:1.5:3 by mass of cement, sand and coarse aggregate respectively, but with the sand content slightly adjusted for each mix in order to maintain a constant cement and coarse aggregate content per 1 m^3 while varying the w/c ratio.

Table 4-1 – Mix proportions used in control study and recorded 28 day strengths

DESIGNATION	W/C	WATER	CEMENT	SAND	COARSE	28 DAY STRENGTH
		kg/m³				MPa
			1	*2*	*4*	
T1	0.4	120	300	779	1200	11.3
T2	0.5	150	300	704	1200	41.4
T3	0.6	180	300	629	1200	39.6
			1	*1.5*	*3*	
T4	0.4	160	400	606	1200	48.4
T5	0.5	200	400	506	1200	49.6
T6	0.6	240	400	406	1200	35.1
			1	*1*	*2*	
T7	0.4	200	500	632	1000	50.0
T8	0.5	250	500	507	1000	48.2
T9	0.6	300	500	382	1000	37.1

The concrete was mixed as described in Chapter 3.2.2.4, and cast in 100x100x500 mm moulds. However, due to the water demand of the 1:2:4 mix combined with the low w/c of 0.4, the workability of the T1 mix was so low that it was not possible to achieve adequate compaction, and therefore the T1 mix was not included for testing. After demoulding, the concrete samples were cured in potable water for 28 days then allowed to air-dry for approximately six months.

A slice of approximately 100x100x15 mm was then taken from the centre of each concrete sample and placed in a carbonation tank at 4% CO_2 for fourteen weeks in order to simulate the carbonation that would have occurred naturally in historic concrete. These slices were then split in half vertically and one-half used for aggregate grading and density tests, while the other half was used for all chemical testing.

The analyses was carried out following BS 1881-124 (British Standards Institution, 2015a), with the exception of density tests which were carried out in accordance with BS EN 12390-7 (British Standards Institution, 2009a), aggregate water absorption tests which were carried out in accordance with BS EN 1097-6 (British Standards Institution, 2013b), and chemically-bound water prior to carbonation, which was estimated using XRF analysis combined with an optimisation process which determined the percentage of chemically bound water by mass of anhydrous cement required to achieve full hydration. A more detailed explanation of each individual test methodology can be found in Chapter 3.3.

4.3.1 Mix Proportion Calculations

4.3.1.1 Aggregate/Binder Content

As the control samples were known to contain no acid-digestible aggregate, aggregate content by mass was assumed to be the insoluble residue content, calculated as per the procedure described in Chapter 3.3.2. The binder content as a % of mass of total concrete was then calculated to the nearest 0.1% as follows:

$$Binder\ content\ \% = 100\% - Aggregate\ content\ \% \tag{25}$$

The aggregate and binder content as a mass in kg per m^3 concrete mix could then be determined from the previously calculated oven-dry density, ρ_{rd}:

$$M_a = \rho_{c.rd} \times \frac{Aggregate\ content\ \%}{100} \tag{26}$$

$$M_b = \rho_{c.rd} \times \frac{Binder\ content\ \%}{100} \tag{27}$$

where:

$\rho_{c.rd}$ is the density of the oven-dried concrete in kg/m^3;

$M_{A.rd}$ is the mass of oven-dried aggregate per m^3 mix in kg;

$M_{B.rd}$ is the mass of oven-dried binder per m^3 mix in kg.

However, it should be noted that the binder content is different from the anhydrous cement content, as the binder content includes the hydrated and carbonated cement of the matrix.

4.3.1.2 Anhydrous Cement Content

LOI was carried out on powdered sub-samples of each specimen. During the LOI test all chemically bound water and carbon dioxide that are part of the binder matrix are driven off by the extreme temperatures, and so the remaining mass is attributed to the anhydrous cement and aggregate. As the overall binder content has been previously calculated, it was then possible to calculate the anhydrous cement content of the concrete:

$$Anhydrous\ cement\ \% = Binder\ content\ \% - LOI\ \% \quad (28)$$

The anhydrous cement content as a mass in kg per 1 m^3 concrete mix could then be determined from the previously calculated oven-dry density, ρ_{rd}:

$$M_{cem} = \rho_{c.rd} \times \frac{Anhydrous\ cement\ \%}{100} \quad (29)$$

where:

$\rho_{c.rd}$ is the density of the oven-dried concrete in kg/m^3;

M_{cem} is the mass of anhydrous cement per m^3 mix in kg.

4.3.1.3 Combined Water Content

The amount of chemically bound water in the cement matrix, also known as the 'combined water', is typically calculated using the procedure detailed in BS 1884-124. However, this test is particularly unsuitable for use with historic concrete as it calculates bound water content from the mass of gas that is driven off at 1000°C and subsequently recaptured in an absorption tube, and, in the case of carbonated concrete, this will inevitably include carbon dioxide as well as water vapour. As the molar mass of CO_2 is over double that of H_2O, 44g/mol compared to 18g/mol respectively, this introduces a significant error which increases with the degree of carbonation. Consequently, a new method of determining chemically bound water content had to be developed for this project.

In this new method, chemical analysis of each specimen was carried out using XRF spectrometry. An XRF analysis was carried out on both a powdered concrete sample and a powdered sample of the insoluble residue from the aggregate content tests. By comparing the results from both these tests an estimation of the chemical composition of the binder could be made.

It was then possible to use an optimisation process to redistribute the calculated amounts of SiO_2, CaO, Al_2O_3, Fe_2O and SO_3 into the potential hydration products and, subsequently, calculate the percentage of water by anhydrous mass of cement that would be required to achieve full hydration. The actual mass of combined water was calculated using the following expression:

$$M_{cw} = M_{cem} \times cw \tag{30}$$

where:

M_{bw} is the mass of combined water per m^3 mix in kg;
M_{cem} is the mass of anhydrous cement per m^3 mix in kg;
cw is the percentage of water by anhydrous mass of cement as a fraction.

However, it should be noted that while this method of calculating chemically bound water content does assume full hydration of the cement, the solution may not be unique and presents a possible source of error.

4.3.1.4 Aggregate Voids Ratio

The aggregate voids ratio was calculated from the results obtained from the aggregate absorption tests carried out in accordance with BS EN 1097-6 (British Standards Institution, 2013b), using the following expression:

$$e_a = \frac{V_{a.w}}{V_{a.s}} = \frac{(M_{a.ssd} - M_{a.rd})/\rho_w}{(M_{a.ssd} - M_{a.im})/\rho_w} \tag{31}$$

where:

e_a is the voids ratio of the aggregate;
$V_{a.w}$ is the volume of aggregate voids filled by water in m^3;
$V_{a.s}$ is the volume of aggregate solids in m^3;
$M_{a.ssd}$ is the mass of the saturated-surface-dried aggregate in kg;
$M_{a.rd}$ is the mass of the oven-dried aggregate in kg;

$M_{a.im}$ is the mass of the saturated sample immersed in water in kg;

ρ_w is the density of water in kg/m^3.

4.3.1.5 Aggregate and Binder Volume

The saturated-surface-dry aggregate mass in kg per m^3 of concrete mix could then also be determined using the previously calculated dry aggregate mass per m^3 of concrete mix and the voids ratio of the aggregate:

$$M_{A.ssd} = M_{A.rd} + e_a \times \rho_w \quad (32)$$

This, as well as the saturated-surface-dry aggregate density – previously determined from the procedure in BS EN 1097-6 (British Standards Institution, 2013b), was then used to calculate the volume of saturated-surface-dry aggregate per m^3 of concrete mix:

$$V_{A.ssd} = M_{A.ssd} \times \rho_{A.ssd} \quad (33)$$

where:

$V_{A.ssd}$ is the volume of saturated-surface-dry aggregate per m^3 mix in m^3;

$M_{A.ssd}$ is the mass of saturated-surface-dry aggregate per m^3 mix in kg;

$\rho_{A.ssd}$ is the density of saturated-surface-dry aggregate per kg/m^3.

Assuming that the remainder of the volume is attributed to the saturated-surface-dry binder, the volume of saturated-surface-dry binder per m^3 of concrete mix was then calculated from the expression:

$$V_{B.ssd} = 1 - V_{A.ssd} \quad (34)$$

where:

$V_{B.ssd}$ is the volume of saturated-surface-dry binder per m^3 mix in m^3.

4.3.1.6 Concrete Voids Ratio

The voids ratio of each hardened concrete samples was calculated from the saturated-surface-dried and oven-dried densities calculated in accordance with BS EN 12390-7 (British Standards Institution, 2009a), using the following expression:

$$e_c = \frac{\rho_{c.ssd} - \rho_{c.rd}}{\rho_w} \quad (35)$$

where:

e_c is the voids ratio of the concrete;

$\rho_{c.ssd}$ is the density of the saturated-surface-dried concrete in kg/m^3;

$\rho_{c.rd}$ is the density of the oven-dried concrete in kg/m^3;

ρ_w is the density of water in kg/m^3.

4.3.1.7 Proportional Share of Concrete Voids

The voids ratio of the binder matrix could be calculated from the proportional share of concrete voids attributed to the binder matrix. However, in order to do this, it was first necessary to calculate the proportion of concrete voids attributed to the aggregate.

Aggregate Proportion of Voids

The aggregate proportion of voids was calculated from the voids ratio of the aggregate and the calculated volume of saturated-surface-dry aggregate in per m^3 mix, using equation (36). As the volume of the saturated-surface-dry aggregate is calculated per m^3 mix, this term can be expressed as a ratio (unitless) as well as a volume (m^3).

$$e_{c.a} = e_a \times V_{A.ssd} \tag{36}$$

where:

$e_{c.a}$ is the proportion of the concrete voids ratio attributed to the aggregate;

e_a is the voids ratio of the aggregate;

$V_{A.ssd}$ is the volume ratio of saturated-surface-dry aggregate per m^3 mix.

Binder Matrix Proportion of Voids

Assuming that the remainder of the concrete voids are found in the binder matrix, the proportion of total concrete voids attributed to it could be calculated from the expression:

$$e_{c.b} = e_c - e_{c.a} \tag{37}$$

where:

e_c is the voids ratio of the concrete;

$e_{c.b}$ is the proportion of the concrete voids ratio attributed to the binder matrix;

$e_{c.a}$ is the proportion of the concrete voids ratio attributed to the aggregate.

4.3.1.8 Binder Matrix Voids Ratio

As with the saturated-surface-dry aggregate, the volume of the saturated-surface-dry binder was calculated per m^3 mix and can, therefore, be expressed as a ratio (unitless) as

well as a volume (m^3). The voids ratio of the binder matrix can be calculated from the expression:

$$e_b = \frac{e_c}{V_{B.ssd}} \quad (38)$$

where:

e_b is the voids ratio of the binder matrix;
e_c is the voids ratio of the concrete;
$V_{B.ssd}$ is the volume ratio of saturated-surface-dry binder per m^3 mix.

4.3.1.9 Free Water Content

The volume of free water was considered to be that which filled the voids of the hardened binder matrix, and was therefore calculated using the expression:

$$V_{fw} = e_b \times V_{B.ssd} \quad (39)$$

where:

V_{fw} is the volume of free water per m^3 mix in m^3;
e_b is the voids ratio of the binder matrix;
$V_{B.ssd}$ is the volume ratio of saturated-surface-dry binder per m^3 mix.

This can then be converted to a mass:

$$M_{fw} = \frac{V_{B.ssd}}{\rho_w} \quad (40)$$

where:

M_{fw} is the mass of free water per m^3 mix in kg;
ρ_w is the density of water in kg/m^3.

4.3.1.10 Total Water Content

If considered to be the sum of combined water and free water, the total water content of each sample could be calculated from the expression:

$$M_{tw} = M_{cw} + M_{fw} \quad (41)$$

where:

M_{tw} is the total mass of water per m^3 mix in kg;

M_{fw} is the mass of free water per m^3 mix in kg;

M_{cw} is the mass of combined water per m^3 mix in kg.

4.3.1.11 Fine and Coarse Aggregate Content

It was possible to determine the fine and aggregate content by measuring the grading of the aggregate following the dry sieving procedure described in BS EN 933-1 (British Standards Institution, 2012b). The fine aggregate was considered to be that which passed through the 4 mm aperture sieve, and the coarse aggregate that which was retained, and the content of each per 1 m^3 mix was determined using the following expressions:

$$M_{Af} = M_{A.rd} \times \frac{M_f}{M_t} \quad (42)$$

$$M_{Ac} = M_{A.rd} \times \frac{M_c}{M_t} \quad (43)$$

where:

M_{Af} is the mass of oven-dried fine aggregate per m^3 mix in kg;

M_{Ac} is the mass of oven-dried coarse aggregate per m^3 mix in kg;

$M_{A.rd}$ is the mass of oven-dried aggregate per m^3 mix in kg;

M_f is the mass of fine aggregate passing through the 4 mm sieve, in kg;

M_c is the mass of coarse aggregate retained on the 4 mm sieve, in kg;

M_t is the total mass of aggregate used in the dry sieving procedure, in kg.

However, it should be noted that each of these masses represents the mass of aggregate only, and does not consider the additional mass of water required to bring the aggregate to a saturated-surface-dry state.

4.3.1.12 Mix Proportion Summary

Once the mix proportions had been calculated, the results could be displayed in a table of standard format with the designed mix proportions (Table 4-4), and the standard and mean deviations determined (Table 4-3). The relevant terms used to represent the specific constituents in the previous mix proportion calculations can be found in Table 4-2:

Table 4-2 – Summary of terms used in calculations and to specify mix proportions

W/C	Water Content	Cement Content	Fine Aggregate	Coarse Aggregate
M_{tw}/M_{cem}	M_{tw}	M_{cem}	M_{Af}	M_{Ac}

4.4 RESULTS

4.4.1 Mix Proportions

Table 4-3 – Summary of deviations of experimental results from actual control mix design

	W/C	WATER CONTENT	CEMENT CONTENT	FINE AGG. CONTENT	COARSE AGG. CONTENT
Mean deviation	0.10	22.9 %	11.1 %	23.5 %	16.3 %
Standard deviation	0.06	12.7 %	12.3 %	14.1 %	5.7 %

Table 4-4 – Comparison of designed and calculated mix proportions

MIX		W/C	WATER	CEMENT	FINE AGG.	COARSE AGG.
			kg/m^3			
T2	*Designed*	0.50	150.0	300.0	704.4	1200.0
	Calculated	0.53	186.2	351.4	767.7	987.5
	Error	0.03	24.1 %	17.1 %	9.0 %	-17.7 %
T3	*Designed*	0.60	180.0	300.0	629.4	1200.0
	Calculated	0.64	222.4	347.3	576.9	1117.7
	Error	0.04	23.6 %	15.8 %	-8.3 %	-6.9 %
T4	*Designed*	0.40	160.0	400.0	605.9	1200.0
	Calculated	0.49	220.8	450.7	712.4	905.4
	Error	0.09	38.0 %	12.7 %	17.6 %	-24.6 %
T5	*Designed*	0.50	200.0	400.0	505.9	1200.0
	Calculated	0.66	279.7	425.3	577.1	980.4
	Error	0.16	39.8 %	6.3 %	14.1 %	-18.3 %
T6	*Designed*	0.60	240.0	400.0	405.9	1200.0
	Calculated	0.67	264.3	397.3	540.2	1020.2
	Error	0.07	10.1 %	-0.7 %	33.1 %	-15.0 %
T7	*Designed*	0.40	200.0	500.0	632.4	1000.0
	Calculated	0.57	280.8	492.9	660.8	882.3
	Error	0.17	40.4 %	-1.4 %	4.5 %	-11.8 %
T8	*Designed*	0.50	250.0	500.0	507.4	1000.0
	Calculated	0.69	263.6	383.6	579.0	924.4
	Error	0.19	5.4 %	-23.3 %	14.1 %	-7.6 %
T9	*Designed*	0.60	300.0	500.0	382.4	1000.0
	Calculated	0.69	306.4	441.9	716.2	713.8
	Error	0.09	2.1 %	-11.6 %	87.3 %	-28.6 %

The deviations of the obtained mix proportions based on the analysis of the concrete samples from the designed mix were significant (Table 4-3, Table 4-4). Furthermore, there does not appear to be any correlation between the mix proportions and the observed deviations – that is to say that no general correlation could be found between the degree of variation in results and specific mix characteristics such as w/c ratio or cement content, suggesting that the errors are due to experimental or sampling errors.

4.4.1.1 Experimental Error

The calculated mix proportions were extremely sensitive to small changes in experimental results. In particular, small variations in density and aggregate content calculations have a significant impact on the accuracy of the results due to the scaling up of the proportions for a 1 m^3 mix. For example, a 10 kg/m^3 increase in oven-dry density resulted in a decrease of up to 0.02-0.03 in the calculated w/c ratio of each sample. This is of particular concern as deviations in calculated density by this margin are common, as the density calculations are themselves particularly sensitive to scaling errors inherent to the use of relatively small test samples.

One particular reason for these errors is the need to weigh the sample in a saturated-surface-dry state – which means that, theoretically, all the pores and voids of the sample are completely saturated with water, but no additional moisture is present on the outer surface. In reality, this is highly unlikely to be the case as the determination that the sample has reached the saturated-surface-dry state is at the discretion of the individual carrying out the test and is based purely on their own perception. This issue is particularly relevant when dealing with small specimens which have a relatively high ratio of surface-layer volume to total volume, and poses the significant risk that small variations in the saturation state of the surface layer will result in density errors which compound as they are used throughout multiple calculations.

The prevalence of this issue can be put into perspective by examining the differences in the results of the density tests. The oven-dry and saturated-surface-dry densities were calculated twice for each of the hardened concrete samples and the results compared. The difference between the two results in each set was recorded and the mean and standard deviations of the error between tests results calculated (Table 4-5). As previously mentioned, adjusting the mix proportion calculations with a 10 kg/m^3 increase in oven-dry density resulted in a decrease of up to 0.02-0.03 in the calculated w/c ratio of each

sample, and this presents a significant issue given that the mean deviation between any two oven-dry density test results for one sample was 10.9 kg/m^3.

Table 4-5 – Summary of deviations of the variation between density test results

	OVEN-DRY DENSITY kg/m^3	SATURATED-SURFACE-DRY DENSITY kg/m^3
Mean deviation	10.9	20.4
Standard deviation	4.8	4.0

Another significant variation that occurred was in the fine, coarse and total aggregate contents. In all cases except sample T9, the total aggregate content was calculated as being lower than the designed mix, and, in all cases except T8, the degree of error between designed and calculated total aggregate contents was significant. While the total aggregate content errors can be attributed to the previously discussed issues inherent to the density calculations, the ratio of both fine and coarse aggregate to total aggregate should not be affected by this.

The fine and coarse aggregate contents as a percentage of total aggregate mass were calculated from the mass of aggregate passing and retained on a 4 mm aperture sieve, respectively. As the sieving procedure required the aggregates to be in an oven-dry state, and the same sample could be retested an unlimited number of times, there is very little error introduced from the actual experimental procedure. As such, it is likely that the errors can be attributed to variations in the physical composition of the concrete. While general sources of physical variations in concrete will be discussed in Chapter 4.4.2, the potential sources of error relating to these specific samples will be discussed at this stage.

As shown in Table 4-7, in all cases except sample T3 the percentage of aggregate passing was significantly greater than expected, and there are several potential reasons this could have occurred: Firstly, once mixing was complete, the fresh concrete was hand trowelled into moulds in layers and it is possible that some segregation occurred in the horizontal plane at this stage – causing the fine and coarse aggregate to be inconsistently positioned throughout the mould, and, as the sawn specimens were relatively thin in one orientation (dimensions approximately 100x100x15 mm), this compositional variation in the horizontal plane would not be taken into consideration by an individual specimen. Secondly, as the sawn specimen was relatively thin, it is possible that a portion of the coarse aggregate that was positioned in the plane of each cut was sawn such that it now passed through the 4 mm aperture sieve and was perceived to be fine aggregate. In

practice, this issue should be minimised by taking cores with a diameter at least three and a half times that of the maximum aggregate size (British Standards Institution, 2012a). However, as previously discussed, it is not always possible to take concrete samples of such size – particularly from historic structures. Thirdly, the concrete samples were heated in a furnace to 400 ± 5°C – as per BS 1881-124 – in order to aid in the break-down of the binder matrix, and this may have resulted in some fragmentation of the aggregate – resulting in an increase of finer particles.

Table 4-6 – Errors in calculated aggregate contents

MIX	FINE AGG.	COARSE AGG.	TOTAL AGG.
	kg/m³		
T2	63.3	-212.5	-149.1
T3	-52.5	-82.3	-134.8
T4	106.5	-294.6	-188.1
T5	71.2	-219.6	-148.4
T6	134.3	-179.8	-45.5
T7	28.4	-117.7	-89.3
T8	71.6	-75.6	-3.9
T9	333.8	-286.2	47.6

Table 4-7 – Variations in percentage of aggregate passing through 4 mm aperture sieve

MIX	PERCENTAGE PASSING 4 MM SIEVE, %		
	DESIGNED	CALCULATED	ERROR
T2	37.0	43.7	6.8
T3	34.4	34.0	-0.4
T4	33.6	44.0	10.5
T5	29.7	37.1	7.4
T6	25.3	34.6	9.3
T7	38.7	42.8	4.1
T8	33.7	38.5	4.9
T9	27.7	50.1	22.4

Table 4-8 – Variations in percentage of aggregate retained on 4 mm aperture sieve

MIX	PERCENTAGE RETAINED 4 MM SIEVE, %		
	DESIGNED	CALCULATED	ERROR
T2	63.0	56.3	-6.8
T3	65.6	66.0	0.4
T4	66.4	56.0	-10.5
T5	70.3	62.9	-7.4
T6	74.7	65.4	-9.3
T7	61.3	57.2	-4.1
T8	66.3	61.5	-4.9
T9	72.3	49.9	-22.4

Table 4-9 – Comparison of errors from aggregate grading and mix proportion calculations

MIX	FINE AGGREGATE, %		COARSE AGGREGATE, %	
	PASSING ERROR	MIX PROPORTION ERROR	RETAINED ERROR	MIX PROPORTION ERROR
T2	6.8	9.0	-6.8	-17.7
T3	-0.4	-8.3	0.4	-6.9
T4	10.5	17.6	-10.5	-24.6
T5	7.4	14.1	-7.4	-18.3
T6	9.3	33.1	-9.3	-15.0
T7	4.1	4.5	-4.1	-11.8
T8	4.9	14.1	-4.9	-7.6
T9	22.4	87.3	-22.4	-28.6

The impact of the density equation errors is again highlighted when comparing the errors obtained during aggregate sieving and aggregate mix proportion calculations, as shown in Table 4-9. One such example is sample T3 which, despite having a negligible error from the aggregate grading, had mix proportion errors of -8.3% and -6.9% for fine and coarse aggregate respectively. Another example of particular note is sample T9 where an error of 22.4% in the aggregate passing the 4 mm aperture sieve resulted in a fine aggregate mix proportion error of 87.3%. These errors occur as a result of the error in total aggregate content which is distributed into fine and coarse aggregate contents using the results from the sieve grading, which in turn increases the error in terms of mass per 1 m^3 mix proportionally, and when this mass error is converted into a percentage error of original mix proportions it can seem particularly high.

Taking these various factors into account, it can be concluded that an accumulation of experimental errors recycled through multiple calculations – particularly those related to density tests – contributed to the significant variation of the estimated mix proportions from the designed mix proportions. Furthermore, the tests used are increasingly inaccurate as the sample size is decreased and this is problematic when dealing with historic concrete structures where limited amounts of material are available for testing.

4.4.2 Porosity

The porosity of concrete is an important factor which affects not only the physical properties of the hardened material – such as surface texture and subsequently the manner and extent to which it will weather – but also influences the mechanical properties – such as shrinkage and creep (detailed in Chapters 2.2 and 2.6). As previously discussed, porosity is determined predominantly by the w/c ratio and curing conditions of the concrete, and, as it has been shown to be difficult to accurately analyse the w/c ratio of historic concrete, it may be necessary to determine the porosity of samples taken from the *in-situ* concrete source if a repair material is to be designed for it. However, there is some debate surrounding the use of current techniques which directly measure porosity and so an investigation was carried out on the control samples T2-T9 – the results of which are shown in Figure 4-1 and Figure 4-2.

Porosity was calculated by two different methods: firstly using MIP as described in Chapter 3.3.8 and, secondly, from the comparison of the results from oven-dried and fully-saturated density tests as described in Chapter 3.3.1. Strictly speaking, the results from density measurements are not a measure of porosity as they inevitably include larger air voids that were not present in the samples used in the MIP analyses. However, as the tests were carried out on laboratory made samples, which were compacted following the standard procedure, the proportion of air voids should be minimal.

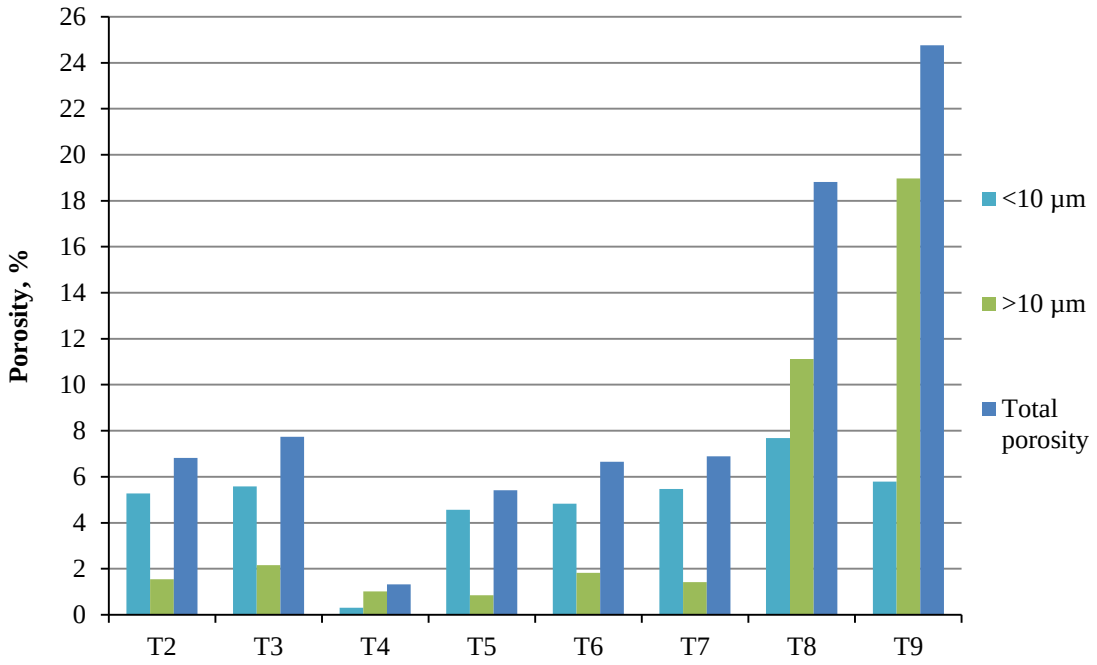

Figure 4-1 – MIP results comparing total porosity and its distribution in pore sizes above and below 10µm

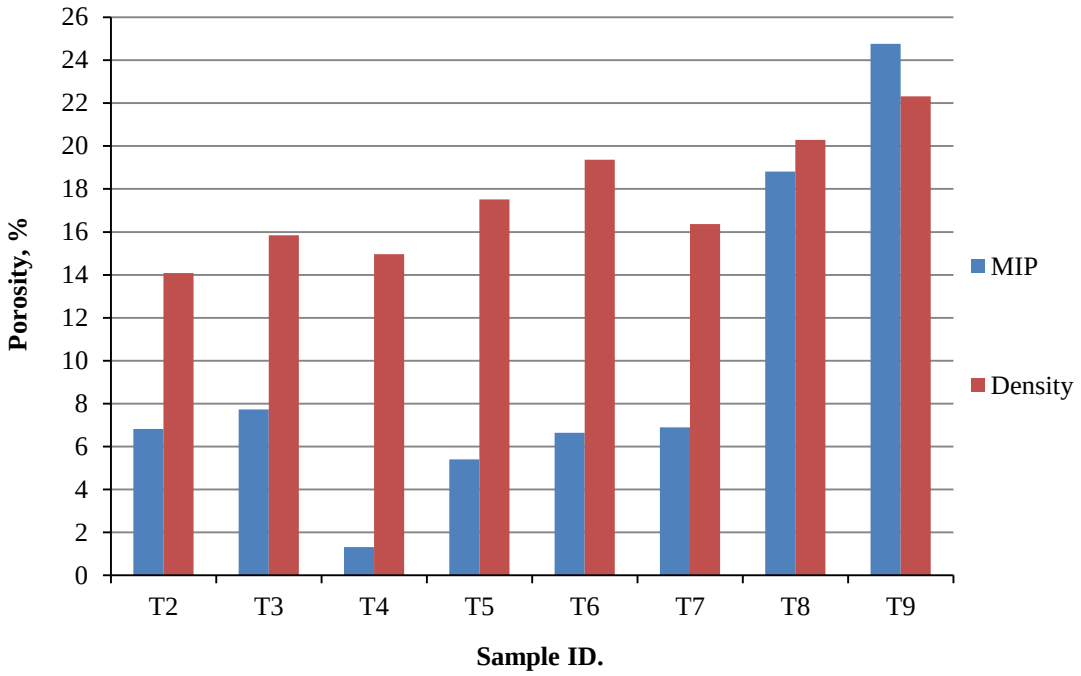

Figure 4-2 – Comparison of total porosity results calculated from MIP and density measurements

There are several factors which influence the porosity of hardened concrete, which need to be considered in the comparison of results. While the effects of hydration on the microstructure of cement paste were discussed in Chapter 2.2.1.3, it is also important to understand that when measuring the porosity of hardened concrete samples, the aggregate type and quantity can also have a significant impact on the porosity results, as can the curing conditions that the concrete was subjected to.

In this study, the same aggregate type was used in each sample and the mix proportions were known – allowing a more accurate interpretation of the results. Furthermore, as the cement type used and curing conditions were the same for each sample, this eliminated two potential sources of variation between the different designed mixes. However, it is still necessary to compare the results of samples which share one equal parameter; in this case comparison is made between the results of samples with the same mix proportions but different w/c ratio (T2/T3, T4/T5/T6, T7/T8/T9), and also between the results of samples with the same w/c ratio but different mix proportions (T4/T7, T2/T5/T8, T3/T6/T9). The mix proportions used can be found in Table 4-1.

In both the density and MIP porosity results, it was clear that for similar cement : sand : aggregate proportions, an increase in w/c ratio resulted in an increase in porosity. There was, however, a discrepancy in the porosity results of the MIP and density tests when comparing samples with the same w/c ratio but different mix proportions. The

expectation was that, at constant w/c ratio, an increase in cement content would result in a higher porosity as the cement matrix is more porous than the aggregate, i.e. in this study, at constant w/c, the 1:1:2 mix would have the greatest porosity and the 1:2:4 mix would have the lowest porosity. While the results of the density tests support this, the MIP results do not as the 1:1.5:3 mixes T5 and T6 have a lower MIP porosity than the corresponding 1:2:4 mixes – T2 and T3 respectively. It is unclear why this is the case.

It could be speculated that this discrepancy may be due to two factors: Firstly, that a significant amount of the coarsest pores in the 1:1.5:3 mix fall outside of the range of measurement of MIP – an issue which is associated with this technique (Taylor, 1997) and was briefly mentioned in Chapter 3.3.8. Secondly, is that this discrepancy may have just arisen as a result of experimental and sampling errors associated with this technique – discussed in detail in the next section of this chapter.

In any case, due to the limited number of tests specimens available from each sample on which these tests were carried out, it is difficult to draw any firm conclusions on this discrepancy. This presents an issue which hinders the usefulness of MIP when trying to ascertain the correlation between particular variables, such as cement composition, on the porosity of historic concrete samples. Given that this couldn't be achieved in a controlled study where the original mix proportions and w/c ratios were known and the variation between samples limited, it is unlikely that, in a *wide-scale* study where all the samples have varying mix proportions, unknown curing conditions, different cement and aggregate types – and where the amount of samples available for destructive testing are limited, the use of MIP will provide any meaningful data.

4.4.2.1 Experimental Error

While porosity tests can provide useful information on the pore structure of laboratory made cement pastes and mortars, there are two important factors which need to be taken into consideration when analysing the data from tests carried out on hardened concrete – particularly that which is carbonated.

Firstly, when the test is carried out on concrete, each sample will inevitably contain varying quantities of cement and aggregate. In order to give a context to results obtained, it is important to have first determined not only the binder and total aggregate contents but also the proportion of fine and coarse aggregates as these will each have different porosities which will affect the results. In the case of the results discussed in this chapter, this issue is of less concern than with concrete taken from an *in-situ* source as the original

mix proportions of these samples were known. However, there will inevitably be a degree of variation from the designed mix proportions due to the heterogeneity of concrete, and this is particularly true when carrying out MIP, as the test is carried out on very small specimens (8 mm diameter cores approximately 15 mm in length) – making it very difficult to ensure that any individual test specimen is, in fact, an accurate representation of the bulk mass with known aggregate and binder contents. Again this issue is of even greater concern when dealing with samples of unknown mix proportions due to the inaccuracies in methods to determine these as discussed earlier in this study.

Secondly, as previously discussed in Chapter 3.3.8, MIP measures pore-entry sizes, not the distribution of pore sizes, and so if large pores can only be accessed through narrow entrances they will be incorrectly registered as smaller pores (Taylor, 1997). This is problematic when dealing with carbonated concrete, as the conversion of calcium hydroxide to calcium carbonate, detailed in Chapter 2.4.1.2, results in an increase in the crystal volume by approximately 11.7% (Ishida & Maekawa, 2001) which in turn causes a decrease in the size of pores in the concrete – causing a finer porosity to be registered during MIP tests.

This creates difficulty when trying to determine the effects of various historic cement compositions on pore structure of cement paste, as even samples with the same cement type and w/c ratio that are carbonated to a different degree may be analysed by MIP as being quite different, due to the effects of carbonation on the pore entry sizes. However, MIP tests may still provide valuable information when analysing an individual concrete sample from a proposed repair area.

While the actual quantification of the range of pore sizes, and indeed the quantification of total porosity, may not be particularly accurate and therefore unsuitable for assessing how a certain cement type will influence the formation of pores in the hardened paste – and subsequently mechanical properties such as shrinkage – it may be that even this analysis of pore entry sizes can provide insight into the physical characteristics of the surface layer of concrete. For example, the results provided by the MIP tests on the pore entry sizes of carbonated concrete may be used to better understand how that material has degraded or will degrade in response to its environment, as discussed in Chapter 2.4.4, and also for comparison with potential repair materials to ensure they will have a similar surface texture and will weather in a similar fashion, as discussed in Chapter 2.6.3.

4.4.3 Variations in the Composition of *In-situ* Concrete

While there are experimental errors that are inherent to concrete testing, it is also important to consider that the heterogeneity of concrete is generally such that, when working with small samples, the overall mix is not being taken into consideration and any test, no matter how accurate, can only give a localised quantitative assessment of composition.

With this in mind, there are several issues related to the *in-situ* casting of fresh concrete which need to be considered when relating the properties of relatively small analytical samples to the much larger parent material – particularly when these samples are derived from one particular area and are unlikely to be representative of bulk material.

Segregation in fresh concrete is a significant factor which contributes to an increase in the variation in the composition of the hardened concrete. It can be attributed to several factors including over-compaction, poor placement and inadequate mix design – the latter is particularly relevant to historic concrete as the first standards for concrete in the UK were not introduced until the first half of the 20th century and even then little attention was paid to the effects of particle size distribution.

A lack of suitable grading is conducive to segregation, which in turn can result in the dense coarse aggregate particles settling to the bottom of the mix and fluid cement paste rising to the top (Neville & Brooks, 2010). The effects of segregation on concrete heterogeneity should not be underestimated, particularly when selecting samples for analysis, as it has been found to result in a difference in cement content of as much as 100 kg/m^3 between the top and bottom of concrete walls and columns (Skinner, 1980).

Bleeding, another form of segregation which occurs in fresh concrete, is usually a result of over-compaction and can have a detrimental effect on concrete as it causes water to rise to the top surface, creating a weak and porous layer in the hardened concrete (Neville & Brooks, 2010) which varies from the underlying material. It can also result in areas of high permeability below large aggregate or reinforcement as the rising water becomes trapped; eventually creating voids in the hardened concrete (Neville & Brooks, 2010)

Segregation is of far more concern when dealing with concrete cast *in-situ* than with concrete cast in a laboratory environment or even cubes taken on a construction site for quality assurance tests. There are two reasons for this: Firstly, when making concrete cubes for laboratory testing, the samples are compacted following a standard procedure –

BS EN 12390-2 (British Standards Institution, 2009b), while concrete cast *in-situ* is compacted to the satisfaction of the concrete finisher, foreman or engineer, and this can result in varying degrees of under or over-compaction – subsequently affecting the heterogeneity of the mix. Secondly, while the control samples used in this study did suffer from some degree of segregation, such as in Figure 4-3, this predominantly results in variations throughout the vertical plane of the sample and, as the samples were sawn parallel to the vertical plane, these variations are contained within the dimensions of the sample which is being tested. When dealing with *in-situ* concrete, it is unlikely that the effects of segregation in the bulk of the concrete will be accurately reflected in samples taken for testing, unless they are vertical cores of the full depth of the concrete.

Figure 4-3 – T9 cross section showing aggregate segregation

Another influencing factor is the 'wall effect'; a physical phenomenon which occurs at the interface of concrete and formwork, where the surface of the formwork affects particle packing by preventing the uniform distribution of coarse aggregate, which in turn causes an increase in the mortar content required to fill the surrounding space (Neville, 2011). This results in the formation of three skin layers: the cement skin, mortar skin and concrete skin – approximately 0.1 mm, 5 mm and 30 mm respectively (Kreijger, 1984), and while the w/c ratio in these layers remains unchanged, both the cement and water content increase (Neville, 2011). Furthermore, some tests have shown that the wall effect can result in an increase in sand content at the concrete surface equal to 10% of the total

mass of aggregate (Neville, 2011; Shacklock, 1959). As such, it is important that any material analysed from the surface skins is not considered to be representative of the concrete in general and, similarly, any material taken from the bulk concrete, such as cores, will not be representative of the surface material.

4.5 CONCLUSIONS

The number of listed concrete structures is increasing and there is a growing need for their conservation and repair. The use of unsuitable proprietary materials has led to poor quality repairs of historically-significant structures in the United Kingdom, some of which have even resulted in physical damage to the historic character of the structure. As a result, the approach to the repair of historic concrete structures has shifted from the use of mass produced proprietary repair materials to purpose made 'like-for-like' replacements.

When analysing any concrete samples with the intention of creating a like-for-like repair material, there are several difficulties associated with scale which need to be taken into consideration. Firstly, as the sample size decreases the analyses become increasingly inaccurate due to the inevitable experimental errors associated with each test, which compound as the results from these tests interact in the various calculations required to determine the original mix proportions – an issue which is particularly prevalent in procedures such as density measurement which the sample to be tested must be in a surface-dry-saturated state. Secondly, concrete is a heterogeneous material and there can be a great deal of variability between small samples taken from different parts of a single mass due to physical phenomena such as segregation, bleeding and the wall effect. As such, it is important to ensure that any samples that are taken from a concrete structure are representative of the area of which analysis is required.

In modern construction practice, these issues are addressed through the analysis of multiple representative samples – often cubes cast for testing and quality conformance purposes at the time of the *in-situ* concrete pour. However, it may not be possible to obtain a similarly representative number or volume of samples from historic concrete structures as they often have a protected status and the amount of material available for testing can be limited. Furthermore, there is currently a lack of clear technical guidance or specification with regards to the analysis and repair of historic concrete structures and the existing standards for analysing hardened concrete are neither accurate for relatively

small samples nor fully suitable for use with chemically or physically damaged historic concrete.

In reality, if we do not possess the means to accurately determine the w/c ratio or the original mix proportions of historic concrete this poses the question: should more focus be placed on developing new analytical methods which can accurately determine the original mix proportions in order to create exact like-for-like replacements?

Given the effects of other factors, such as curing conditions and the degree of hydration, on the microstructure and mechanical properties of hardened concrete it may, in reality, be more effective to undertake a more in-depth study of the *in-situ* material, and to try to replicate its physical properties as closely as possible through a series of trials. In any case, it is essential to apply the knowledge that concrete is a heterogeneous material to each repair situation and to be aware of the potential causes of variation.

5 REVIEW OF HISTORIC TEST DATA

5.1 INTRODUCTION

As previously discussed, there is very limited published data regarding the nature of Portland cement and other constituents in historically-significant concrete structures in Scotland or the wider United Kingdom. Furthermore, there was a lack of suitable material available for testing as part of the historic sample study in Chapter 6.

Therefore, as part of this project, several government agencies, private companies and independent testing houses were approached to ascertain whether they possessed any historical records or reports from tests which had been carried out on concrete structures pre-dating 1950 and, if so, if it was possible to study these to obtain additional data.

Unfortunately, in most cases, the response was negative – with most of the contacts reporting no such testing records. The exception was Transport Scotland who provided access to the historic test reports from structures in their care that had previously been assessed.

5.2 METHODOLOGY

In total, there were reports for 36 structures pre-dating 1950 – carried out by 8 different testing houses, in which a total of 119 samples were analysed. These reports included visual analyses of concrete cores, as well as the test results for cover to reinforcement, the degree of carbonation, chemical analyses, compressive strength and density at various saturation states.

Cover to reinforcement, compressive strength, hardened density and chemical analyses were determined in accordance with BS 1884-204 (British Standards Institution, 1988a), BS 1881-120 (British Standards Institution, 1983a), BS 1181-114 (British Standards Institution, 1983b), BS 1181-124 (British Standards Institution, 1988b) and BS 4551 (British Standards Institution, 1980) respectively.

The results of these tests are summarised in the tables on pages 124-139, with the exception of cover to reinforcement which can be found in the tables on pages 140-142. The results of the covermeter survey are listed separately as these were carried out *in-situ*, while the results of the other tests were carried in a laboratory on test specimens which had been removed from the designated structure.

5.3 RESULTS

Table 5-1 – Summary of results from historic test reports, part 1 of 12

	Allt Molach					Achosregan		Allt Na H Achlaise		
Code	A82 670					A828 120		A82 650		
Construction Year	1931					1900		1931		
Report Year	1984					1991		1984		
Testing House	St. Albans					Stangers		St. Albans		
As Received Density, *kg/m³*	-	-	-	-	-	2380	2410	-	-	-
Saturated Density, *kg/m³*	2390	2380	2390	2370	2330	2400	2420	2310	2260	2270
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	77 .1	79.5	72.3	57.3	59.9	26.0	34.0	25.6	18.0	45.9
Estimated Cube Strength, *N/mm²*	78.5	81.0	67.5	53.5	56.0	25.5	32.5	26.0	18.5	43.5
Insoluble Residue, *%*	-	79.54	-	75.20	-	-	-	-	82.30	80.45
Soluble Silica (SiO_2), *%*	-	3.60	-	4.43	-	-	-	-	3.10	3.96
Calcium Oxide (CaO), *%*	-	8.92	-	10.50	-	-	-	-	7.34	8.13
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	0.23	-	0.26	-	-	-	-	0.35	0.26
Cement Content, *%*	-	13.8	-	16.3	-	-	-	-	11.4	12.6
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	-	-	-	-	-	Fair	Fair	-	-	-
Voids, *%*	1.5	1.0	1.5	1.5	1.5	1.0	1.0	2.0	3.0	1.5
Honeycombing	-	-	-	-	-	-	-	-	-	-
Cracks	-	-	-	-	-	-	-	-	-	-
Aggregate Distribution	-	-	-	-	-	Even	Even	-	-	-
Maximum Aggregate Size, mm	55	75	63	46	59	-	-	36	37	45
Mix Proportions	-	1 : 5.8	-	-	-	-	-	-	1 : 7.3	1 : 6.5

Table 5-2 – Summary of results from historic test reports, part 2 of 12

	Allt Na H Achlaise	Altrua					Ashaig		Auch	
Code	A82 650	A82 1070					A87 330		A82 615	
Construction Year	1931	1927					1938		1930	
Report Year	1984	1982					1997		1993	
Testing House	St. Albans	St. Albans					Highland Council		Saynor	
As Received Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Saturated Density, *kg/m³*	2390	2302	2306	2355	2403	-	2376	2377	2450	2360
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	36.1	23.6	33.0	41.6	54.12	-	36.0	30.0	35·5	23-0
Estimated Cube Strength, *N/mm²*	33.5	22.0	32.5	39.5	51.5	-	38.0	31.5	35·5	23-0
Insoluble Residue, *%*	-	82.10	79.20	79.40	80.00	70.90	-	-	-	-
Soluble Silica (SiO_2), *%*	-	3.33	3.94	3.81	3.98	4.59	-	-	-	-
Calcium Oxide (CaO), *%*	-	8.15	9.24	9.64	9.61	10.90	-	-	-	-
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	0.26	0.41	0.29	0.28	0.45	-	-	-	-
Cement Content, *%*	-	12.6	14.3	15.0	14.9	16.9	-	-	10.1	16.9
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	-	-	-	-	-	-	Good	Good	Even	Even
Voids, *%*	1.5	8.0	10.0	30.0	2.5	-	0.5	0.5	0·5	3·0
Honeycombing	-	-	-	-	-	-	-	-	None	None
Cracks	-	-	-	-	-	-	-	-	None	None
Aggregate Distribution	-	-	-	-	-	-	-	-	Even	Even
Maximum Aggregate Size, *mm*	38	40	35	45	60	-	20	20	-	-
Mix Proportions	-	1 : 6.5	1 : 5.5	1 : 5.3	1 : 5.4	1 : 4.2	-	-	-	-

Table 5-3 – Summary of results from historic test reports, part 3 of 12

	Auchendrain						Brora River		Bunan	
Code	A83 130						A9 1695		A87 340	
Construction Year	1937						1928		1938	
Report Year	1991						1991		1997	
Testing House	Stangers						Stangers		Highland Council	
As Received Density, *kg/m³*	2400	2360	2420	2380	2380	2380	2450	2450	-	-
Saturated Density, *kg/m³*	2400	2360	2430	2400	2370	2390	2450	2450	2347	2381
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	51.5	57.5	61.0	53.0	55.0	63.5	52.0	39.5	47.0	22.0
Estimated Cube Strength, *N/mm²*	52.5	60.5	59.0	50.5	57.5	65.5	50.5	38.0	49.5	23.0
Insoluble Residue, *%*	-	-	-	-	-	-	-	-	-	-
Soluble Silica (SiO_2), *%*	-	-	-	-	-	-	-	-	-	-
Calcium Oxide (CaO), *%*	-	-	-	-	-	-	-	-	-	-
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	-	-	-	-	-	-	-	-	-	-
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	Good	Good	Fair	Good	Good	Good	Good	Good	Good	Good
Voids, *%*	0.5	0.5	1.0	0.5	0.5	0.5	0.0	0.5	0.5	0.0
Honeycombing	-	-	-	-	-	-	-	-	-	-
Cracks	-	-	-	-	-	-	-	-	-	-
Aggregate Distribution	Even	Even	Even	Even	Even	Even	Even	Even	-	-
Maximum Aggregate Size, *mm*	-	-	-	-	-	-	-	-	20.0	20.0
Mix Proportions	-	-	-	-	-	-	-	-	-	-

Table 5-4 – Summary of results from historic test reports, part 4 of 12

	Cairnie				**Clynemilton Burn**		**Croe Water**			
Code	A96 340				A9 1710		A83 50			
Construction Year	1937				1931		1940			
Report Year	1995				1991		1991			
Testing House	Grampian Council				Stangers		Stangers			
As Received Density, *kg/m³*	2600	2620	2650	2640	2320	2330	2420	2420	2420	2420
Saturated Density, *kg/m³*	-	-	-	-	2320	2340	2420	2420	2420	2420
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	80.0	77.5	86.5	83.0	22.5	43.5	43.5	39.0	34.5	35.5
Estimated Cube Strength, *N/mm²*	73.5	71.5	80.0	76.5	21.5	41.5	45.0	39.5	30.0	34.5
Insoluble Residue, *%*	-	-	-	-	-	-	-	-	-	-
Soluble Silica (SiO_2), *%*	-	-	-	-	-	-	-	-	-	-
Calcium Oxide (CaO), *%*	-	-	-	-	-	-	-	-	-	-
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	-	-	-	-	-	-	-	-		-
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	Good	Good	Good	Good	Fair	Fair	Good	Good	Good	Good
Voids, *%*	0.0	0.0	0.0	0.0	1.5	1.0	0.5	0.5	0.5	0.5
Honeycombing	-	-	-	-	-	-	-	-	-	-
Cracks	None	None	None	None	-	-	-	-	-	-
Aggregate Distribution	Even	Even	Even	Even	Even	Even	Even	Even	Even	Even
Maximum Aggregate Size, *mm*	20	20	20	20	-	-	-	-	-	-
Mix Proportions	-	-	-	-	-	-	-	-	-	-

Table 5-5 – Summary of results from historic test reports, part 5 of 12

	Croe Water						Ferniehirst			Fhithich
Code	A83 50						A68 30			A82 1380
Construction Year	1940						1926			1933
Report Year	1991						1996			1985
Testing House	Stangers						Saynor			Site Services
As Received Density, *kg/m³*	2420	2490	2470	2470	2470	2430	-	2400	2420	-
Saturated Density, *kg/m³*	2440	2500	2490	2500	2490	2440	2510	2430	2420	2300
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	2170
Compressive Strength of Core, *N/mm²*	37.5	46.0	48.0	54.5	50.0	34.5	59·5	38.5	54.0	36.0
Estimated Cube Strength, *N/mm²*	36.0	49.0	455.0	54.0	48.0	35.0	34·5	37.5	52.0	36.0
Insoluble Residue, *%*	-	-	-	-	-	-	-	77.84	77.48	-
Soluble Silica (SiO_2), *%*	-	-	-	-	-	-	-	4.07	3.84	-
Calcium Oxide (CaO), *%*	-	-	-	-	-	-	-	10.30	10.25	11.4
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	5.17	5.47	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	-	-	-	-	-	-	16.3	16.0	15.9	16.2
Estimated Water : Cement Ratio	-	-	-	-	-	-	0.40	-	-	-
Compaction	Good	Good	Good	Good	Good	Good	Even	Good	Good	-
Voids, *%*	0.5	0.5	0.5	0.0	0.0	0.5	0.0	0.0	0.5	1.5
Honeycombing	-	-	-	-	-	-	None	-	-	-
Cracks	-	-	-	-	-	-	None	-	-	-
Aggregate Distribution	Even	Even	Even	Even	Even	Even	Even	Even	Even	Even
Maximum Aggregate Size, *mm*	-	-	-	-	-	-	-	-	-	20
Mix Proportions	-	-	-	-	-	-	-	-	-	1 : 4.9

Table 5-6 – Summary of results from historic test reports, part 6 of 12

	Golspie Big Burn		Inchbonny						Kinchrackine West	
Code	A91 660		A68 50						A85 470	
Construction Year	1939		1926						1933	
Report Year	1991		1996						1993	
Testing House	Stangers		Saynor						Saynor	
As Received Density, *kg/m³*	2300	2300	-	2380	2400	2520	2370	2368	-	-
Saturated Density, *kg/m³*	2300	2320	2490	2390	2400	2530	2390	2358	2350	2380
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	45.5	40.5	37.5	20.5	22.0	23.5	21.0	18.5	30.0	33.0
Estimated Cube Strength, *N/mm²*	43.5	38.0	34.5	20.0	21.0	22.0	20.5	16	30.0	33·0
Insoluble Residue, *%*	-	-	-	-	-	-	-	-	-	-
Soluble Silica (SiO_2), *%*	-	-	-	-	-	-	-	-	-	-
Calcium Oxide (CaO), *%*	-	-	-	-	-	-	-	-	-	-
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	-	-	15.8	-	-	-	-	-	9.5	10.2
Estimated Water : Cement Ratio	-	-	0.66	-	-	-	-	-	-	-
Compaction	Good	Good	Even	Poor	Poor	Good	Fair	Poor	Even	Even
Voids, *%*	0.5	0.5	0.0	3.0	4.0	0.5	1.0	4.0	0.5	0·5
Honeycombing	-	-	None	-	-	-	-	-	None	None
Cracks	-	-	None	-	-	-	-	-	None	None
Aggregate Distribution	Even	Even	Even	Even	Even	Even	Even	Poor	Even	Even
Maximum Aggregate Size, *mm*	-	-	-	-	-	-	-	-	-	-
Mix Proportions	-	-	-	-	-	-	-	-	-	-

Table 5-7 – Summary of results from historic test reports, part 7 of 12

	Kinglas									
Code	A83 70									
Construction Year	1932									
Report Year	1991									
Testing House	Stangers									
As Received Density, *kg/m³*	2280	2270	2310	2350	2300	2350	2270	2300	2330	2330
Saturated Density, *kg/m³*	2290	2270	2320	2360	2310	2350	2270	2300	2340	2330
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	38.0	27.0	52.5	33.5	64.5	48.5	49.5	51.5	61.5	57.5
Estimated Cube Strength, *N/mm²*	39.5	26.5	54.5	35.5	67.0	50.5	52.0	54.0	60.0	56.0
Insoluble Residue, *%*	-	-	-	-	-	-	-	-	-	-
Soluble Silica (SiO_2), *%*	-	-	-	-	-	-	-	-	-	-
Calcium Oxide (CaO), *%*	-	-	-	-	-	-	-	-	-	-
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	-	-	-	-	-	-	-	-	-	-
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	Fair	Fair	Fair	Good	Good	Good	Fair	Good	Good	Good
Voids, *%*	1.5	2.0	1.0	0.5	0.5	0.5	1.0	0.5	0.5	0.5
Honeycombing	-	-	-	-	-	-	-	-	-	-
Cracks	-	-	-	-	-	-	-	-	-	-
Aggregate Distribution	Even	Fair	Even	Even	Even	Even	Even	Even	Even	Even
Maximum Aggregate Size, *mm*	-	-	-	-	-	-	-	-	-	-
Mix Proportions	-	-	-	-	-	-	-	-	-	-

Table 5-8 – Summary of results from historic test reports, part 8 of 12

	Kinlochlaich								Kintradwell Burn	
Code	A828 110								A9 1720	
Construction Year	1939								1918	
Report Year	1991								1991	
Testing House	H. Stanger								Stangers	
As Received Density, *kg/m³*	-	-	-	-	-	-	-	-	2320	2340
Saturated Density, *kg/m³*	2470	2400	2530	2450	2410	2400	2460	2530	2330	2360
Oven Dried Density, *kg/m³*	2370	2280	2440	2360	2310	2310	2360	2430	-	-
Compressive Strength of Core, *N/mm²*	33.1	19.6	37.9	37.6	33.1	39.1	20.3	33.8	45.0	59.5
Estimated Cube Strength, *N/mm²*	36.0	22.0	40.0	41.0	36.0	39.0	22.0	35.0	47.5	63.0
Insoluble Residue, *%*	76.79	87.42	79.52	77.87	-	-	-	-	-	-
Soluble Silica (SiO_2), *%*	2.61	2.19	3.33	3.75	-	-	-	-	-	-
Calcium Oxide (CaO), *%*	7.70	6.73	8.81	8.53	-	-	-	-	-	-
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	0.39	0.27	0.48	-	-	-	-	-	-	-
Cement Content, *%*	11.9	10.4	13.7	13.2	-	-	-	-	-	-
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	-	-	-	-	-	-	-	-	Good	Good
Voids, *%*	-	-	-	-	-	-	-	-	0.0	0.0
Honeycombing	-	-	-	-	-	-	-	-	-	-
Cracks	-	-	-	-	-	-	-	-	-	-
Aggregate Distribution	-	-	-	-	-	-	-	-	Even	Even
Maximum Aggregate Size, *mm*	-	-	-	-	-	-	-	-	-	-
Mix Proportions	1 : 6 : 3	1 : 8 : 3	1 : 5 : 8	1 : 5 : 9	-	-	-	-	-	-

Table 5-9 – Summary of results from historic test reports, part 9 of 12

	Lagain		Latheron	Leacann				Leitiri		
Code	A82 1180		A9 1900	A83 140				A82 1080		
Construction Year	1932		1937	1937				1927		
Report Year	1997		1994	1991				1982		
Testing House	Highland Council		Stangers	Stangers				St. Albans		
As Received Density, *kg/m³*	-	-	2340	2300	2260	2330	2270	-	-	-
Saturated Density, *kg/m³*	2275	2268	2350	2300	2280	2330	2310	-	-	2245
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	34.0	24.5	37.0	25.0	29.5	39.0	36.5	-	-	31.15
Estimated Cube Strength, *N/mm²*	35.5	26.0	35.0	24.5	28.0	37.0	38.0	-	-	31.0
Insoluble Residue, *%*	-	-	58.68	-	-	-	-	73.19	75.07	78.80
Soluble Silica (SiO_2), *%*	-	-	3.32	-	-	-	-	4.40	4.43	4.23
Calcium Oxide (CaO), *%*	-	-	19.18	-	-	-	-	10.72	10.65	9.77
Loss on Ignition at 925°C, *%*	-	-	14.80	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	0.42	0.38	-
Cement Content, *%*	-	-	16.4	-	-	-	-	16.6	16.5	15.1
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	Poor	Poor	Good	Fair	Fair	Fair	Good	-	-	-
Voids, *%*	5.0	5.0	0.0	1.0	1.5	1.0	0.5	-	-	10.0
Honeycombing	-	-	None	-	-	-	-	-	-	-
Cracks	-	-	None	-	-	-	-	-	-	-
Aggregate Distribution	-	-	Even	Even	Even	Even	Even	-	-	-
Maximum Aggregate Size, *mm*	20	20	-	-	-	-	-	-	-	35
Mix Proportions	-	-	-	-	-	-	-	-	-	-

Table 5-10 – Summary of results from historic test reports, part 10 of 12

	Leitiri			Marchburn		Nant				Occumster
Code	A82 1080			A76 160		A85 130				A99 30
Construction Year	1927			1936		1938				1936
Report Year	1982			1994		1991				1993
Testing House	St. Albans			Saynor		Stangers				Stangers
As Received Density, *kg/m³*	-	-	-	-	-	2390	2410	2450	2380	2300
Saturated Density, *kg/m³*	2308	2414	2382	2320	2380	2390	2410	2450	2380	2300
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-		-	-
Compressive Strength of Core, *N/mm²*	27.84	52.19	53.42	18.0	28.0	55	55	50.5	34	44.0
Estimated Cube Strength, *N/mm²*	26.0	52.0	50.5	16.5	26.0	57	56	45.5	34	41.5
Insoluble Residue, *%*	81.50	80.10	79.20	-	-	-	-	-	-	68.88
Soluble Silica (SiO_2), *%*	3.36	3.87	4.13	-	-	-	-	-	-	4.60
Calcium Oxide (CaO), *%*	8.61	9.00	9.59	-	-	-	-	-	-	13.22
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	9.37
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	13.4	14.0	14.9	-	-	-	-	-	-	18.1
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	-	-	-	Even	Even	Good	Good	Good	Good	Fair
Voids, *%*	7.0	4.0	20.0	2.0	0·5	0.5	0.5	0.5	0.5	1.5
Honeycombing	-	-	-	Small Pockets	None	-	-	-	-	-
Cracks	-	-	-	None	None	-	-	-	-	-
Aggregate Distribution	-	-	-	Even	Even	Even	Even	Even	Even	Even
Maximum Aggregate Size, *mm*	60	55	50	-	-	-	-	-	-	-
Mix Proportions	-	1 : 5.7	1 : 5.3	-	-	-	-	-	-	-

Table 5-11 – Summary of results from historic test reports, part 11 of 12

	Oich		Sandhole						Sheriffmill	
Code	A82 1220		A83 150						A96 470	
Construction Year	1932		1938						1942	
Report Year	1995		1991						1991	
Testing House	Site Services		Stangers						Sandberg	
As Received Density, *kg/m³*	-	-	2240	2310	2180	2200	2400	2390	-	-
Saturated Density, *kg/m³*	2360	2390	2240	2310	2210	2220	2420	2420	-	-
Oven Dried Density, *kg/m³*	2265	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	47.5	53.5	17.5	37.0	22.0	27.5	45.0	47.0	-	-
Estimated Cube Strength, *N/mm²*	47.5	54.0	16.5	34.5	22.5	27.5	46.5	48.5	-	-
Insoluble Residue, *%*	-	-	-	-	-	-	-	-	-	-
Soluble Silica (SiO_2), *%*	-	-	-	-	-	-	-	-	3.7	3.33
Calcium Oxide (CaO), *%*	9.2	-	-	-	-	-	-	-	9.07	8.06
Loss on Ignition at 925°C, *%*	-	-	-	-	-	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	-	-	-	-	-
Cement Content, *%*	12.8	-	-	-	-	-	-	-	14.1	12.5
Estimated Water : Cement Ratio	-	-	-	-	-	-	-	-	-	-
Compaction	-	-	Poor	Good	Good	Good	Good	Fair	-	-
Voids, *%*	0.5	0.5	4.0	0.5	0.5	1.0	0.5	1.0	-	-
Honeycombing	-	-	Honeycombed section in core	-	-	-	-	-	-	-
Cracks	-	-	-	-	-	-	-	-	-	-
Aggregate Distribution	Even	Even	Even	Even	Even	Even	Even	Even	-	-
Maximum Aggregate Size, *mm*	20	20	-	-	-	-	-	-	-	-
Mix Proportions	1 : 6.6	-	-	-	-	-	-	-	-	-

Table 5-12 – Summary of results from historic test reports, part 12 of 12

	Sitheinn		Station Bridge	Study	Tulla				
Code	A82 1170		A68 11	A82 740	A82 640				
Construction Year	1932		1926	1931	1931				
Report Year	1997		1996	1994	1984				
Testing House	Highland Council		Saynor	Stangers	St. Albans				
As Received Density, *kg/m³*	-	-	-	-	-	-	-	-	-
Saturated Density, *kg/m³*	2361	2380	2466	-	2362	2410	2334	2386	2320
Oven Dried Density, *kg/m³*	-	-	-	-	-	-	-	-	-
Compressive Strength of Core, *N/mm²*	49.0	51.5	32.5	-	32.1	36.3	28.1	37.4	28.1
Estimated Cube Strength, *N/mm²*	52.0	53.5	31. 6	-	31.0	34.0	26.5	35.0	26.5
Insoluble Residue, *%*	-	-	-	75.68	-	82.90	82.80	-	-
Soluble Silica (SiO_2), *%*	-	-	-	2.81	-	2.71	2.67	-	-
Calcium Oxide (CaO), *%*	-	-	-	8.26	-	7.14	7.07	-	-
Loss on Ignition at 925°C, *%*	-	-	-	9.22	-	-	-	-	-
Sulphur Trioxide (SO_3), *%*	-	-	-	-	-	0.23	0.18	-	-
Cement Content, *%*	-	-	16.8	12.8	-	11.1	11.0	-	-
Estimated Water : Cement Ratio	-	-	0.72	-	-	-	-	-	-
Compaction	Good	Good	Even	-	-	-	-	-	-
Voids, *%*	0.5	0.5	0.0	-	1.0	0.5	2.0	1.0	0.5
Honeycombing	-	-	None	-	-	-	-	-	-
Cracks	-	-	None	-	-	-	-	-	-
Aggregate Distribution	-	-	Even	-	-	-	-	-	-
Maximum Aggregate Size, *mm*	20	20	-	-	30	35	25	35	25
Mix Proportions	-	-	-	-	-	1 : 2.9 : 4.6	1 : 3.5 : 4.0	-	-

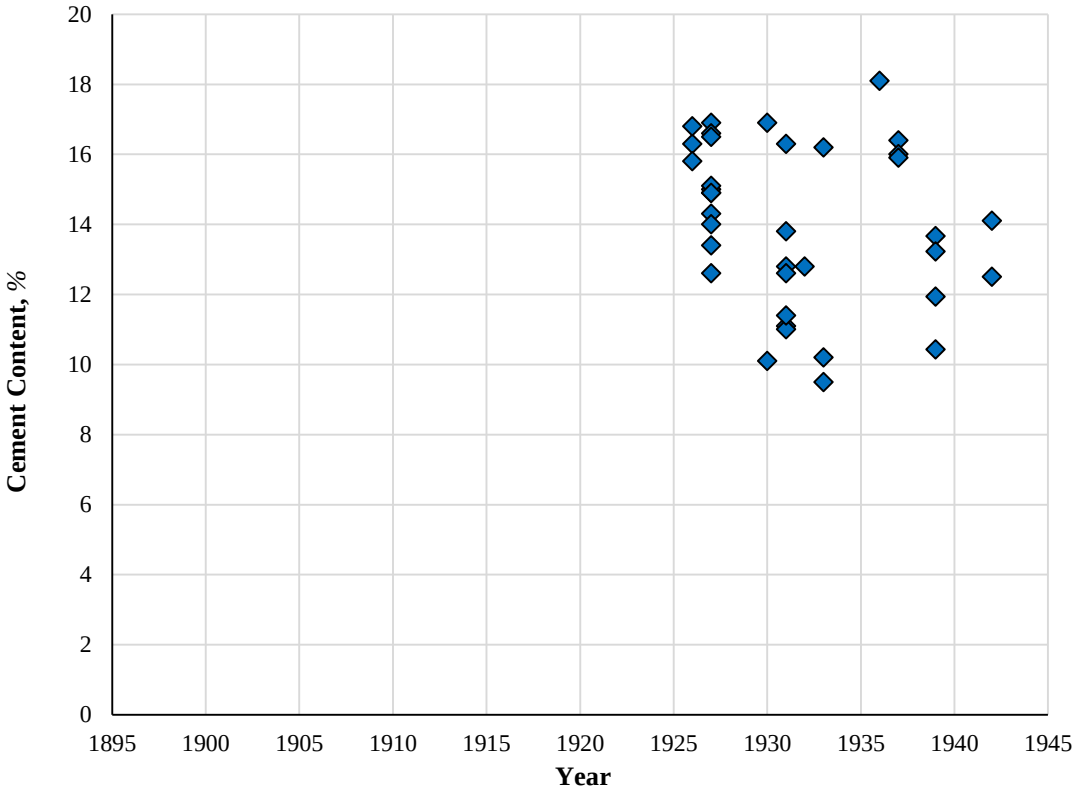

Figure 5-1 – Summary of cement contents of concrete samples by construction year

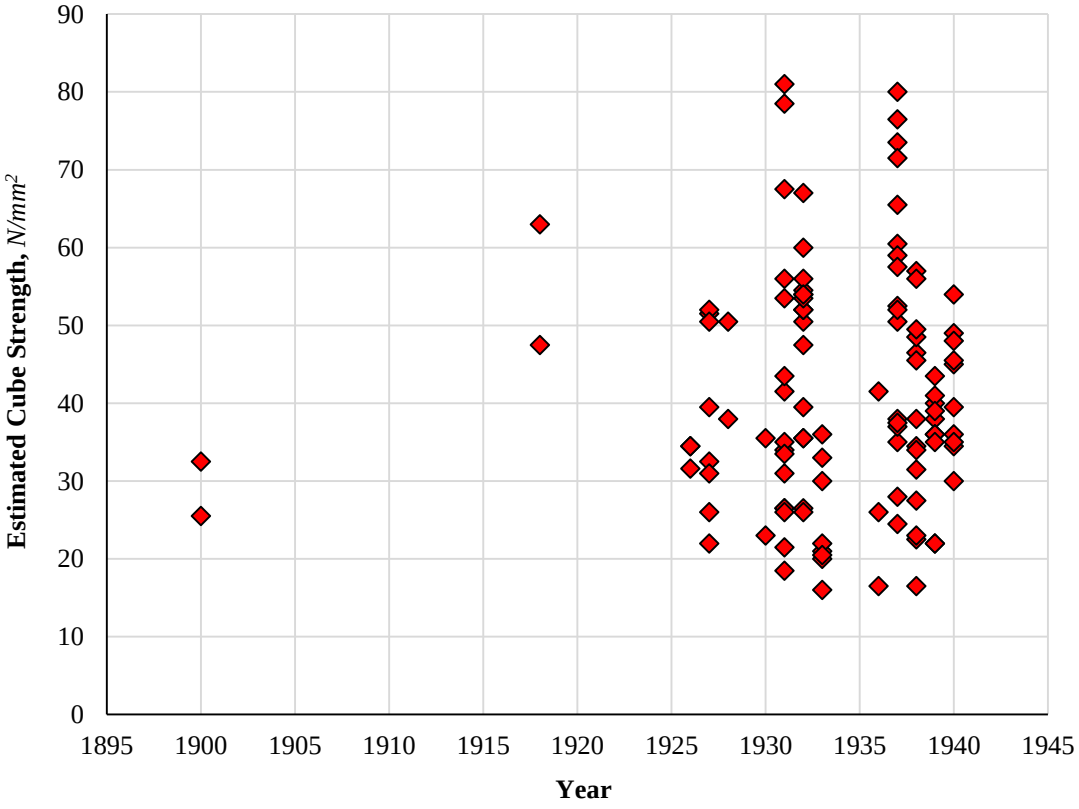

Figure 5-2 – Summary of estimated cube strengths of concrete samples by construction year

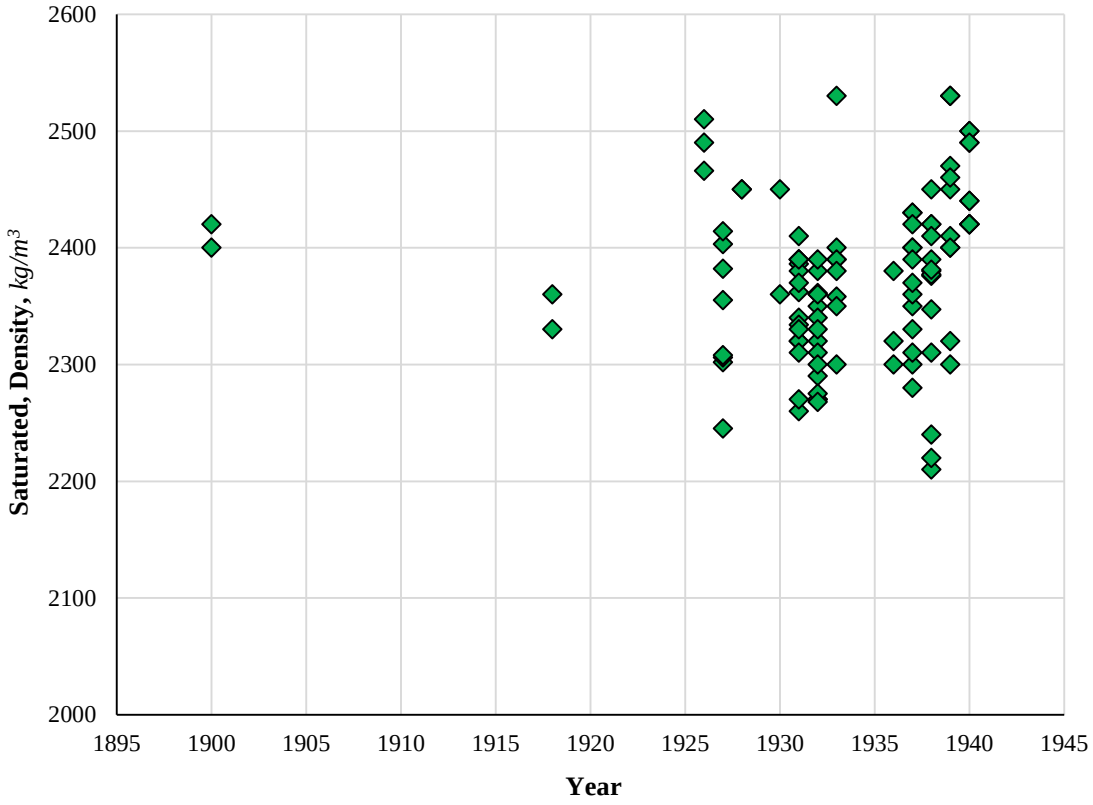

Figure 5-3 – Summary of saturated densities of concrete samples by year

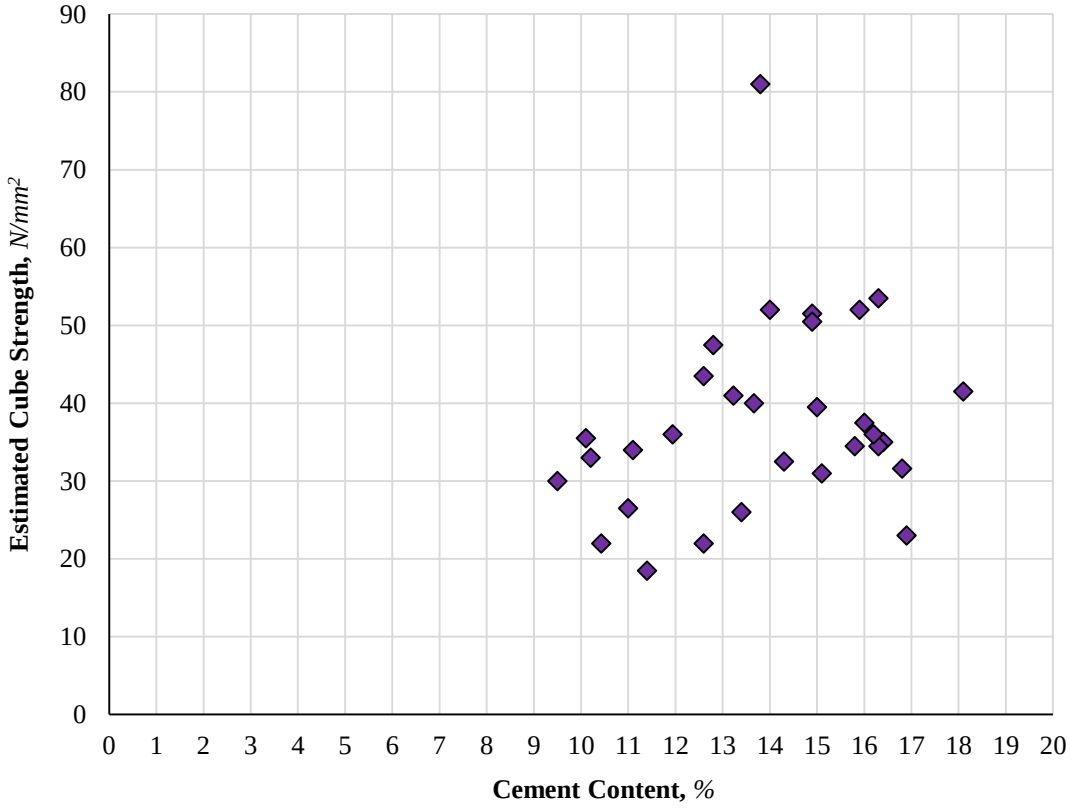

Figure 5-4 – Summary of estimated cube strengths of concrete samples by cement content

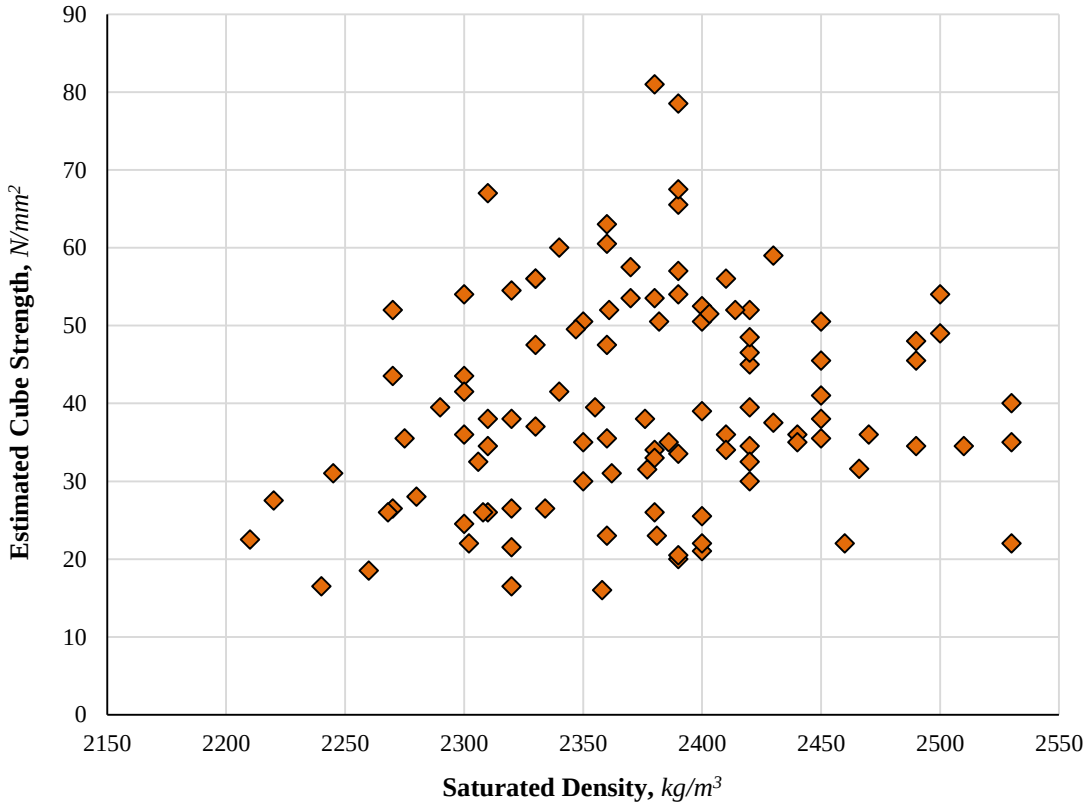

Figure 5-5 – Summary of estimated cube strengths of concrete samples by saturated density

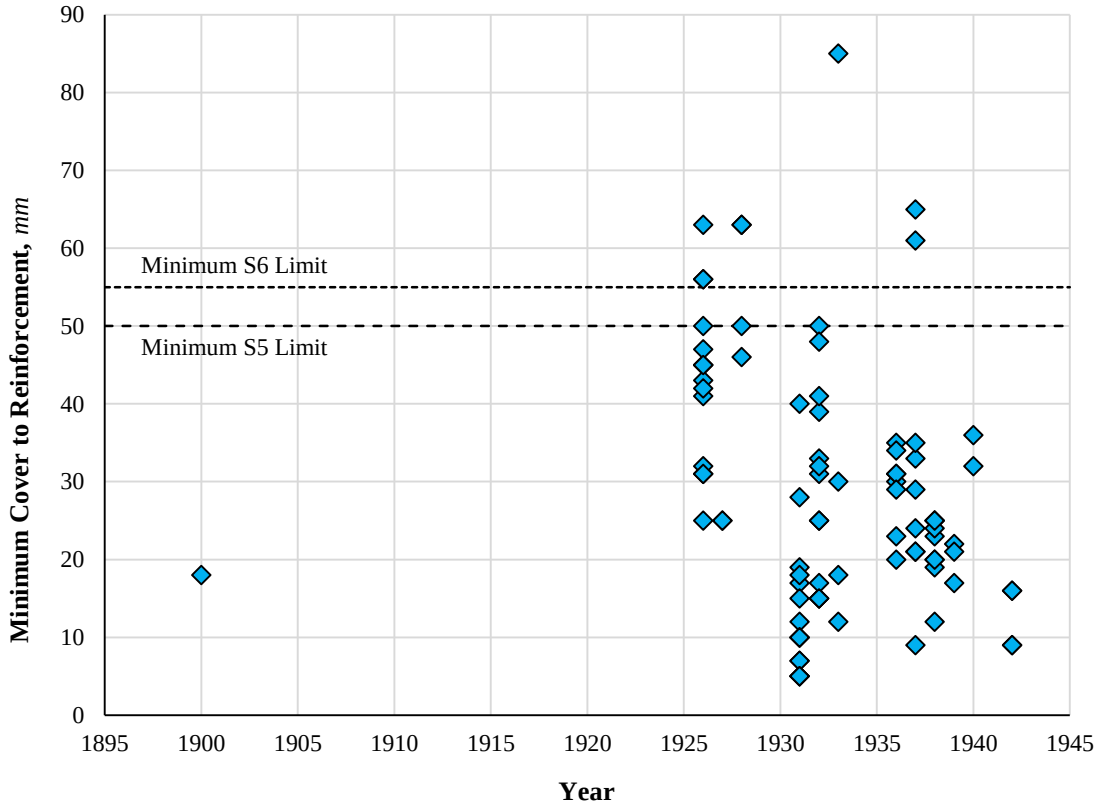

Figure 5-6 – Summary of minimum concrete cover to steel reinforcement by year

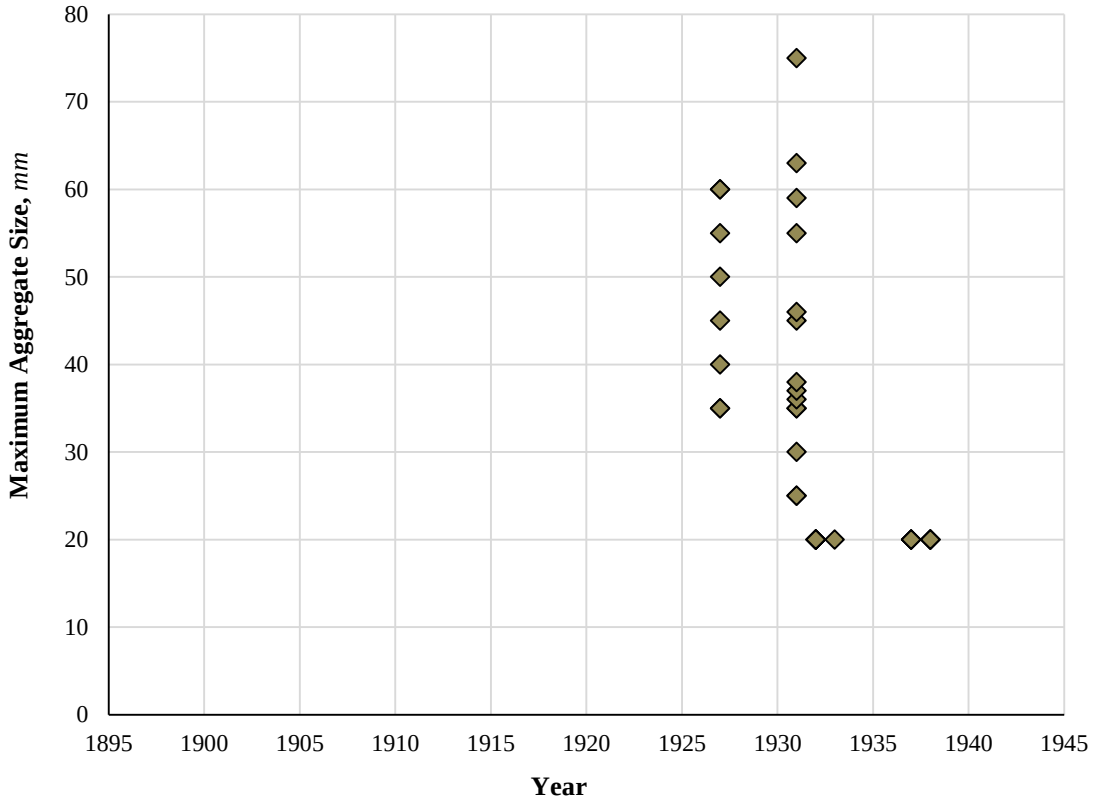

Figure 5-7 – Summary of maximum aggregate size by year

Table 5-13 – Summary of historic test results from Transport Scotland reports

	CEMENT CONTENT	ESTIMATED CUBE STRENGTH	MAX. AGG. SIZE	SATURATED DENSITY	MIN. COVER
	%	*N/mm^2*	*mm*	*kg/m^3*	*mm*
Maximum	18.1	81.0	75.0	2530	85
Minimum	9.5	16.0	20.0	2210	5
Mean	14.0	41.1	34.7	2374	29
Median	14.1	38.0	35.0	2380	25
Standard Deviation	2.3	15.0	15.8	69	16.3
Mean Deviation	1.9	12.3	13.2	55	12.9
No. of Test Results	37	113	37	109	90

Table 5-14 – Summary of cover meter survey results, part 1 of 3

	YEAR	ELEMENT	MIN. COVER	MAX. COVER
			mm	*mm*
Allt Molach	1931	*A*	12	30
Achosregan	1900	*A*	18	56
Allt Na H Achlaise	1931	*A*	5	50
		B	10	20
		C	7	40
		D	10	20
		E	5	50
		F	7	20
		G	5	50
Altrua	1927	*A*	25	48
Ashaig	1938	*A*	20	30
		B	25	30
		C	19	27
Auch	1930	-	-	-
Auchendrain	1937	*A*	9	46
Brora River	1928	*A*	63	75
		B	63	90
		C	50	81
		D	46	57
Bunan	1938	*A*	23	30
		B	25	30
		C	20	26
Cairnie	1937	*A*	61	67
		B	21	42
		C	21	40
Clynemilton Burn	1931	*A*	17	49
		B	19	147
Croe Water	1940	*A*	36	120
		B	32	136
Ferniehirst	1926	*A*	56	125
		B	63	110
		C	45	80
		D	56	115
		E	25	42
Fhearchair	1937	*A*	65	70
		B	33	36

Table 5-15 – Summary of cover meter survey results, part 2 of 3

	YEAR	ELEMENT	MIN. COVER	MAX. COVER
			mm	*mm*
Fhithich	1933	*A*	85	96
Golspie Big Burn	1939	*A*	17	67
		B	22	52
		C	21	36
Inchbonny	1926	*A*	45	115
		B	50	86
		C	47	79
		D	41	135
		E	43	62
Inverlochy	1933	*A*	18	193
		B	12	145
Kinchrackine West	1933	*A*	30	50
Kinglas	1932	*A*	15	38
		B	33	77
		C	39	85
Kinlochlaich	1939	-	-	-
Kintradwell Burn	1918	-	-	-
Lagain	1932	*A*	15	30
		B	25	34
		C	25	36
Latheron	1937	*A*	29	33
		B	35	48
Leacann	1937	*A*	24	65
Leitiri	1927	*A*	25	50
Marchburn	1936	*A*	20	50
		B	30	56
		C	35	54
		D	31	54
Nant	1938	*A*	24	68
		B	25	65
Occumster	1936	*A*	31	37
		B	23	39
		C	34	39
		D	29	36
Oich	1932	*A*	50	56
		B	48	52
		C	41	52
		D	31	38

Table 5-16 – Summary of cover meter survey results, part 3 of 3

	YEAR	ELEMENT	MIN. COVER	MAX. COVER
			mm	*mm*
Sandhole	1938	*A*	12	47
Sheriffmill	1942	*A*	9	-
		B	9	-
		C	16	-
		D	16	-
Sitheinn	1932	*A*	17	30
		B	15	32
		C	32	42
Station Bridge	1926	*A*	45	60
		B	31	57
		C	42	75
		D	32	54
		E	31	70
Study	1931	*A*	40	46
		B	15	31
		C	28	53
Tulla	1931	*B*	5	40
		C	10	28
		D	18	35

5.3.1 Format of Test Reports

The general format of the test reports was inconsistent between the different testing houses, with each one carrying out slightly different tests and sometimes working to different standards for the same tests. For example, in some cases chemical analysis was carried out following BS 1181-124 *'Testing concrete. Methods for analysis of hardened concrete'* and in others BS 4551 *'Methods of testing mortars, screeds and plasters'* was used. In either case, neither of these standard is ideal as they cannot be used to accurately assess concrete which is physically or chemically damaged – as discussed in Chapter 4. Furthermore, the calculation used in these standards require certain assumptions to be made about the initial chemical composition of the cement and these are based on the soluble silica and calcium oxide contents of, what was at that time, the current specification for Portland cement – not of the actual historic Portland cement being analysed.

Another inconsistency in the test reports was the reporting of density, which was usually measured in the 'saturated' state (109 recorded), but with some 'as-received' (63) and 'oven-dried' (10) densities also recorded. Ideally, the reports would contain a

measurement of both oven-dried and saturated density, however, it is understandable that oven-dried density was the least recorded – particularly when dealing with limited sample size, as oven-drying should not be undertaken on samples which need to be tested to determine their compressive strength or chemical composition. The use of as-received density is, itself, not a particularly useful metric for assessing hardened concrete as it is a value which varies with the saturation level of the concrete which inevitably changes depending on the original moisture conditions of the concrete, method of sample removal, storage conditions after removal and the time between removal and testing. This is particularly true of concrete cores, as removing these requires a coring rig which applies a steady flow of up to ten litres of water per 100 mm diameter core of 300 mm length, in order prevent the barrel from jamming due to overheating and to remove debris from around the barrel (Baker, 1992).

Finally, while aggregate is a crucial constituent of concrete and has a significant impact on its physical properties, there is very little in terms of aggregate results. Of the 119 samples tested, only 37 had even a recorded maximum aggregate size. Even fewer (18) had cement to aggregate proportions and, of these, only six had proportions of cement to fine and coarse aggregate – the other 12 reports contained only a cement to total aggregate ratio. Again this is not ideal as the grading of the aggregate plays a critical role in the structure and properties of hardened concrete.

5.3.2 Trends in Results

From this data, there seems to be no link between factors such as cement content, compressive strength, density and minimum cover to reinforcement, and the year in which the structure was built. However, this is not unexpected, as each of the structures would have been designed with specific requirements in mind.

While there does seem to be a general trend of increasing compressive strength with increasing cement content, the lack of chemical composition data for the cements and the lack of aggregate size and grading data mean that any conclusions about this relationship would be tenuous at best.

5.3.2.1 Maximum Aggregate Size

One interesting trend, which can be clearly observed in Figure 5-7, is the sudden change in maximum aggregate size after 1932. Of the 37 samples analysed, all 15 of the samples that date from after 1932 had a maximum aggregate of only 20 mm, and this perhaps signifies a change in design practice which limited the maximum size of aggregate – in

particular, this change coincides with the release of the first edition of Reynolds' *'Reinforced Concrete Designers' Handbook'* (1932). While Reynolds' handbook was not legislation, it did specify recommendations for the grading of aggregate for various types of concrete. Furthermore, Reynolds suggested that, for ordinary building work, the fine aggregate should be graded from dust to ¼ in. (6.35 mm) particles, and the coarse aggregate from ¼ in. to ¾ in. (19.0 mm) particles – with permissible coarse aggregate sizes of 1½ in. (38.1 mm) or 2 in. (50.8 mm) for mass concrete works (Reynolds, 1932).

In all the test results from structures built prior to 1932, the maximum aggregate size was extremely variable, with the largest maximum aggregate size being 75 mm, the smallest being 25 mm and the mean being 45 mm, and the use of aggregates of this size is likely to have a negative impact on the composition and physical properties of hardened concrete. While there was no aggregate grading results included in the reviewed reports, it is likely that the use of such large maximum aggregate sizes would have resulted in poor grading of the aggregate in general, which, in turn, can cause segregation and bleeding, as discussed in Chapter 4.4.3.

Furthermore, in the modern construction practice in United Kingdom, the maximum aggregate size for structural concrete is usually 25 mm or 40 mm as it has to be at least 5 mm smaller than the horizontal bar spacing and at least 2/3 smaller than the vertical bar spacing (Neville & Brooks, 2010) in order to be evenly distributed through the hardened concrete. This is unlikely to have occurred in these historic concrete mixes.

While it is unclear when exactly this issue became known to engineers designing reinforced concrete structures, it appears this was certainly of concern by the 1930s. Writing in his 1938 book *'Practical Reinforced Concrete Design'*, Reynolds references the by-laws for the construction and conversion of buildings in reinforced concrete – found in the '*The London Building (Amendment) Act, 1935'*, which restricted the size of coarse aggregate to at least ¼ in. (6.35 mm) less than the minimum lateral distance between reinforcing bars (Reynolds, 1938).

Aggregate of this size is also likely to have detrimental effect on concrete as, the larger the aggregate particle, the larger the interfacial transition zone (ITZ) between the cement paste and the aggregate surface. The ITZ is an area in which the 'wall effect' from coarse aggregate alters the way in which cement particle packing occurs against the aggregate surface and results in an area of high porosity (Scrivener, *et al.*, 2004). This ITZ becomes

increasingly porous as the aggregate size increases (Basheer, *et al*., 2005) – resulting in a significant area of weakness in hardened concrete.

Based on these results, it seems that, in general, the maximum aggregate size was not well controlled in historic concrete mixes or its implications on the properties of hardened properties well understood.

5.3.3 Comparison with Modern Concrete Design Standards

As discussed in Chapter 2.3, there were very few design standards during early reinforced concrete construction – the first appearing in 1915 (Addis & Bussell, 2003) – and so designs were carried out by individual specialists who each had their own requirements, and had only to satisfy the occasional independent consultant.

Furthermore, many aspects of concrete design which have a significant impact on durability were not well understood or overlooked completely. Writing in his 2001 paper, titled *'Consideration of durability of concrete structures: Past present, and future',* Neville discusses the historic belief that existed within the engineering community that concrete durability was inherently related to its strength and that, as a result of this belief, even in the 1960s it was generally believed that concrete durability itself did not need to be considered at the design stage (Neville, 2001).

This view has altered significantly over time and, in modern construction in the United Kingdom, concrete structures are designed in accordance with BS EN 1992 '*Eurocode 2: Design of Concrete Structures'* (British Standards Institution, 2014b), and with concrete conforming to BS EN 206 (British Standards Institution, 2013c). These standards specify the design requirements that concrete structures must adhere to in order to ensure the durability of the concrete in specific environments – known as 'exposure classes'. For each given exposure class – described in Table 5-17 – these design requirements include, but are not limited to:

- Maximum w/c ratio
- Minimum strength class
- Minimum cement content
- Minimum cover to steel reinforcement

While the minimum strength class of concrete is a factor which seems to have always been of principal concern in concrete design, it appears from Neville's paper (2001) that

the influence of w/c ratio and cement type on durability were not fully appreciated until the 1980s. The effects of these on the microstructure of hardened cement paste was discussed in Chapter 2.2, and, in Eurocode 2, these are controlled by the recommended limiting values specified in Table 5-18. However, the minimum cover is also an important requirement of the concrete design which, as described in BS EN 1992-1-1 (British Standards Institution, 2014b), serves to ensure:

- The safe transmission of bond forces
- The protection of steel against corrosion
- Adequate fire resistance

In this discussion, it is the minimum cover to steel reinforcement as a factor in the protection of steel against corrosion that is of most concern. While the methods of concrete deterioration were discussed in Chapter 2.4 and the impact of inadequate cover described in 2.4.2.1, there has, so far, been no discussion in this thesis of the method for determination of the minimum requirement for concrete cover to steel reinforcement.

Given the lack of historic design requirements for durability and the critical role that minimum cover plays in determining the durability of reinforced concrete structures, it is useful, at this stage, to compare the data from the tests reports to the modern design requirements in order to give a clearer context to their significance. However, in order to do this effectively, it is first necessary to give a brief overview of the process which determines the minimum design requirements.

5.3.3.1 Design Overview

Exposure Class

The determination of exposure class is critical in the design of reinforced concrete structures, as the environmental exposure conditions will determine the methods and extent of deterioration that will occur. Taking this into consideration at the design stage, as is required by Eurocode 2, means that engineers specify a design criterion that provides adequate protection to ensure the durability of any given structure throughout its intended service life.

The relevant exposure class is selected from those designated in BS EN 206-1 (British Standards Institution, 2013c) and BS 1992-1-1 (British Standards Institution, 2014b) – reproduced in Table 5-17. Once this has been determined, the relevant recommended

limiting values for maximum w/c ratio, minimum strength class and minimum cement content can be found in BS EN 206-1 – reproduced in Table 5-18. In the event that more than one exposure class is relevant to the structure, the engineer should specify the most severe of each value i.e. the lowest w/c and the highest minimum strength class and cement content.

Strength Class

The strength class of normal-weight concrete is designated by the code '*C X/Y*', where X and Y represent the 28-day compressive strength of a standard cylinder and the 28-day-compressive strength of a standard cube, respectively, of that specific concrete mix design. In the United Kingdom, the recommended minimum and maximum strength values for concrete bridges, as described in BS EN 1992-2 (British Standards Institution, 2005), are C30/37 and C70/85 respectively. The full list of standard compressive strength classes, as designated in BS EN 206 (British Standards Institution, 2013c), can be found in Table 5-19. However, it should be noted that, in some cases, the minimum requirements of strength class to ensure durability may result in a choice of a higher strength class than is required for the structural design (British Standards Institution, 2014b).

It is worth noting that, while 28-day strength has become the traditional standard metric for the characterisation of concrete strength, Neville (2011) points out that there is no particular scientific significance to choice of 28 days and that it is simply an age that has allowed a significant period of hydration to have taken place and, as it is divisible by 7, it was probably originally selected so that, consequently, casting and testing would always both fall on a traditional working day.

Due to the changes in the fineness and C_3S content of Portland cement – discussed in Chapter 2.2 – the rate of hydration of modern Portland cement is much greater than that of historic Portland cement (Neville, 2011) but, due to the decrease in C_2S, the long-term strength gain – that which occurs after 28 days – is much lower than would be observed in the historic material. This means that a direct comparison of historic 28-day strengths with modern 28-day strength requirements is not necessarily fair, as it is not an accurate reflection of the ultimate strength of the concrete. Furthermore, due to the undocumented changes and variations in historic Portland cement composition, it is also impossible to make any predictions of the ultimate strength from 28-day strength records.

Structural Class

The determination of structural class is made with the assumption that strength class and w/c are related values (British Standards Institution, 2014b) and that, consequently, the strength class is also related to the permeability of a hardened concrete. Eurocode 2 recognises six structural classes (S1 – S6), and, In the United Kingdom, the recommended structural class for a designed working life of 50 years is S4 (British Standards Institution, 2014b), with recommended modifications as per Table 5-20. These modifications take into account not only the aforementioned strength class and exposure conditions, but also the design working life of the structure, the geometry of the member and if any control procedures that are in place to ensure the quality of the concrete.

Minimum Cover Due to Environmental Conditions

Once the structural class and exposure conditions have been established, the minimum cover with regards to durability for reinforced steel can be determined using Table 5-21 – reproduced from BS EN 1992-1-1 (British Standards Institution, 2014b). As previously mentioned, in accordance with Eurocode 2, minimum cover has to be determined not only to ensure the protection of the steel against corrosion, but also the safe transmission of bond forces and adequate fire resistance. Each of these minimum cover requirements is calculated separately and the greatest value satisfying all three should be selected.

5.3.3.2 Determining Minimum Requirements

In the case of the structures analysed in the Transport Scotland reports, as they were all elements of road bridges, the exposure classes XC4, XD3 and XF4 are all applicable. Based on this and the recommended values in Table 5-18, the minimum requirements in all cases can be determined to be:

- Maximum w/c = 0.45 (XD3, XF4)
- Minimum strength class = C35/45 (XD3)
- Minimum cement content = 340 kg/m^3 (XF4)

The minimum structural class for concrete bridges is S4, but, as these bridges have all exceeded a 50-year design life, the structural class needs to be increased by two. It is unlikely that any special quality control of concrete production matching today's requirements was ensured in these instances and while it's possible that the member slab geometry may result in a potential reduction in structural class, there is not information available to make that discernment.

However, it is possible that each individual structure or element may qualify for a reduction in structural class if the results of the compressive strength tests are assumed to be indicative of its strength class and this exceeds the requirements for structural class reduction specified in Table 5-20. In any case, the structural class is likely to be S5 or S6 and, with regards to the exposure classes previously specified, the minimum cover with regards to durability for each structural class can be determined to be:

- Minimum cover for S5 = 50 mm (XD3)
- Minimum cover for S6 = 55 mm (XD3)

5.3.3.3 Comparison with Minimum Requirements

Unfortunately, due to gaps in the test data and the general difficulties in accurately calculating the w/c and cement content of hardened concrete, as discussed in Chapter 4, it is not possible to compare the results of the Transport Scotland tests with modern concrete design standards. However, it is possible to compare the results of the covermeter survey with recommended minimum cover for durability, and, while there is no record of 28-day strengths for the concrete samples, the results of the compressive tests can be compared to the current standards to determine which, if any, of the samples have a characteristic compressive strength that is greater than the minimum 28-day requirement.

Concrete Cover to Reinforcement

The results of the covermeter survey – shown in the tables on pages 140-142 and Figure 5-6 on page 138 – show that the minimum recorded cover, in most cases, was significantly lower than even the S5 requirement of 50 mm. In fact, of the 90 recorded minimum cover results, 79 (87.7%) were below the 50 mm requirement and, of the 86 recorded maximum cover results, 39 (43.3%) were below the 50 mm requirement. If the structural class is considered to be S6, then 82 (91.1%) of the recorded minimum results and 52 (57.7%) of the maximum recorded results were below the minimum cover requirement of 55 mm. Of all the results, the minimum recorded was only 5 mm and the mean was 18 mm.

Overall, these results are concerning, as they show that most of these structures are inadequately designed to protect the steel reinforcement from corrosion due to carbonation and chloride ingress. Furthermore, they show the extent to which engineers historically lacked an understanding of the crucial role that concrete cover has in ensuring the durability of reinforced concrete, and this is likely to be an issue of concern, not only

in these structures, but to reinforced concrete structures in Scotland, and the wider United Kingdom, in general.

Compressive Strength

While 71 (62.8%) of the 113 reported compressive strength test results on cores were greater than the minimum requirement of 35 N/mm^2, only 43 (38.1%) of the estimated cube strengths were greater than the minimum requirement of 45 N/mm^2. The reason for this discrepancy is probably that the compressive strength tests were carried out on cores of varying sizes – not of the standard size. Therefore, different correction factors were applied to these results based on the dimensions of the tested core. As such, it is the corrected values of estimated cube strength that should be considered for comparison.

These results are concerning for two reasons – both of which have previously been touched on. Firstly, and most obviously, 61.9% of the structures – all of which are over 50 years old – do not have a characteristic compressive strength that is adequate in terms of durability requirements by modern concrete design standards. Secondly, since the rate of hydration of historic Portland cements was much lower than in modern Portland cement, the rate at which it has taken each concrete sample to reach its current strength is much longer. This means that the permeability of the concrete cover layer was likely higher for a more prolonged duration of time than would be observed in a concrete structure of the same tested strength using modern Portland cement – on which these minimum design requirements are based.

Table 5-17 – Exposure classes

Class designation	Description of the environment	Informative examples where exposure classes may occur
1 No risk of corrosion or attack		
X0	For concrete without reinforcement or embedded metal: all exposures except where there is freeze/thaw, abrasion or chemical attack For concrete with reinforcement or embedded metal: very dry	Concrete inside buildings with very low air humidity
2 Corrosion induced by carbonation		
XC1	Dry or permanently wet	Concrete inside buildings with low air humidity Concrete permanently submerged in water
XC2	Wet, rarely dry	Concrete surfaces subject to long-term water contact Many foundations
XC3	Moderate humidity	Concrete inside buildings with moderate or high air humidity External concrete sheltered from rain
XC4	Cyclic wet and dry	Concrete surfaces subject to water contact, not within exposure class XC2
3 Corrosion induced by chlorides		
XD1	Moderate humidity	Concrete surfaces exposed to airborne chlorides
XD2	Wet, rarely dry	Swimming pools Concrete components exposed to industrial waters containing chlorides
XD3	Cyclic wet and dry	Parts of bridges exposed to spray containing chlorides Pavements Car park slabs
4 Corrosion induced by chlorides from sea water		
XS1	Exposed to airborne salt but not in direct contact with sea water	Structures near to or on the coast
XS2	Permanently submerged	Parts of marine structures
XS3	Tidal, splash and spray zones	Parts of marine structures
5. Freeze/Thaw Attack		
XF1	Moderate water saturation, without de-icing agent	Vertical concrete surfaces exposed to rain and freezing
XF2	Moderate water saturation, with de-icing agent	Vertical concrete surfaces of road structures exposed to freezing and airborne de-icing agents
XF3	High water saturation, without de-icing agents	Horizontal concrete surfaces exposed to rain and freezing
XF4	High water saturation with de-icing agents or sea water	Road and bridge decks exposed to de-icing agents Concrete surfaces exposed to direct spray containing de-icing agents and freezing Splash zone of marine structures exposed to freezing
6. Chemical attack		
XA1	Slightly aggressive chemical environment according to EN 206-1, Table 2	Natural soils and ground water
XA2	Moderately aggressive chemical environment according to EN 206-1, Table 2	Natural soils and ground water
XA3	Highly aggressive chemical environment according to EN 206-1, Table 2	Natural soils and ground water

Source: Reproduced from BS EN 1992-1-1:2004+A1:2014 (British Standards Institution, 2014b) and BS EN 206:2013 (British Standards Institution, 2013c)

Table 5-18 – Recommended limiting values for composition and properties of concrete

	Exposure classes																	
	No risk of corrosion or attack	Carbonation-induced corrosion				Chloride-induced corrosion						Freeze/thaw attack				Aggressive chemical environments		
						Sea water			Chloride other than from sea water									
	X0	XC 1	XC 2	XC 3	XC 4	XS 1	XS 2	XS 3	XD 1	XD 2	XD 3	XF 1	XF 2	XF 3	XF 4	XA 1	XA 2	XA 3
Maximum w/c[c]	–	0,65	0,60	0,55	0,50	0,50	0,45	0,45	0,55	0,55	0,45	0,55	0,55	0,50	0,45	0,55	0,50	0,45
Minimum strength class	C12/15	C20/25	C25/30	C30/37	C30/37	C30/37	C35/45	C35/45	C30/37	C30/37	C35/45	C30/37	C25/30	C30/37	C30/37	C30/37	C30/37	C35/45
Minimum cement content[c] (kg/m^3)	–	260	280	280	300	300	320	340	300	300	320	300	300	320	340	300	320	360
Minimum air content (%)	–	–	–	–	–	–	–	–	–	–	–	–	4,0[a]	4,0[a]	4,0[a]	–	–	–
Other requirements	–	–	–	–	–	–	–	–	–	–	–	Aggregate in accordance with EN 12620 with sufficient freeze/thaw resistance				–	Sulfate-resisting cement[b]	

[a] Where the concrete is not air entrained, the performance of concrete should be tested according to an appropriate test method in comparison with a concrete for which freeze/thaw resistance for the relevant exposure class is proven.

[b] Where sulfate in the environment leads to exposure classes XA2 and XA3, it is essential to use sulfate-resisting cement conforming to EN 197-1 or complementary national standards.

[c] Where the *k*-value concept is applied the maximum *w/c* ratio and the minimum cement content are modified in accordance with 5.2.5.2.

Source: Reproduced from BS EN 206:2013, Table F.1 (British Standards Institution, 2013c)

Table 5-19 – Compressive strength classes for normal-weight and heavy-weight concrete

COMPRESSIVE STRENGTH CLASS	MINIMUM CHARACTERISTIC CYLINDER STRENGTH AT 28 DAYS *N/mm²*	MINIMUM CHARACTERISTIC CUBE STRENGTH AT 28 DAYS *N/mm²*
C8/10	8	10
C12/15	12	15
C16/20	16	20
C20/25	20	25
C25/30	25	30
C30/37	30	37
C35/45	35	45
C40/50	40	50
C45/55	45	55
C50/60	50	60
C55/67	55	67
C60/75	60	75
C70/85	70	85
C80/95	80	95
C90/105	90	105
C100/115	100	115

Source: Reproduced from BS EN 206:2013 (British Standards Institution, 2013c)

Table 5-20 – Recommended structural classification modifications

STRUCTURAL CLASS MODIFICATIONS							
CRITERION	EXPOSURE CLASS						
	X0	XC1	XC2/XC3	XC4	XD1	XD2/XS1	XD3/XS2/XS3
Design working life of 100 years	increase class by 2	increase class by 2	increase class by 2	increase class by 2	increase class by 2	increase class by 2	increase class by 2
Strength class	≥C30/37 reduce class by 1	≥C30/37 reduce class by 1	≥C35/45 reduce class by 1	≥C40/50 reduce class by 1	≥C40/50 reduce class by 1	≥C40/50 reduce class by 1	≥C45/55 reduce class by 1
Member with slab geometry	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1
Special quality of production ensured	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1	reduce class by 1

Source: Reproduced from BS EN 1992-1-1:2004+A1:2014 (British Standards Institution, 2014b)

Table 5-21 – Values of minimum cover requirements with regard to durability of reinforced steel

REQUIREMENT FOR MINIMUM COVER *(mm)* DUE TO ENVIRONMENTAL CONDITIONS							
STRUCTURAL CLASS	EXPOSURE CLASS						
	X0	XC1	XC2/XC3	XC4	XD1/XS1	XD2/XS2	XD3/XS3
S1	10	10	10	15	20	25	30
S2	10	10	15	20	25	30	35
S3	10	10	20	25	30	35	40
S4	10	15	25	30	35	40	45
S5	15	20	30	35	40	45	50
S6	20	25	35	40	45	50	55

Source: Reproduced from BS EN 1992-1-1:2004+A1:2014 (British Standards Institution, 2014b)

5.4 CONCLUSIONS

Due to the lack of material available for testing, test data was collated from reports previously submitted to Transport Scotland by eight different testing houses. These test reports contained data for 119 samples from 36 different structures which were built prior to 1950. The laboratory test data from each of these samples was recorded and, in combination with further data from 90 *in-situ* covermeter surveys previously carried out across these structures, analysed in order to try and establish a greater understanding of historic concrete construction in Scotland.

The approach to testing and reporting of results between the different testing houses varied and while most reports focussed primarily on the compressive strength of concrete cores removed from the structures, there was a lack of additional data relating to the physical and chemical composition of the concrete. Unfortunately, this lack of supporting compositional data made it made it difficult to observe trends which may exist in the methods of design and construction of concrete structures prior to 1950. However, there were two clear conclusions that could be drawn from these test reports.

The first was that the maximum aggregate size in the mixes was not well controlled, and so it is likely that the effect that the maximum aggregate size has on the properties of hardened concrete was not well understood. It would seem from the test data that this changed in 1932 – the same year that the first edition of Reynolds' *'Reinforced Concrete Designers' Handbook'* (1932) was published – as, in all of the analysed concrete samples that were cast after this time, the maximum aggregate size was found to be 20 mm only.

The second conclusion is that, from a durability standpoint, most of these structures are inadequately designed when compared to modern building standards. In particular there is a concerning lack of protective concrete cover to reinforcement, with at least 87.7% of the areas surveyed having a cover less than the 50 mm minimum requirement and in some cases the depth of cover was determined to be low as 5 mm. Furthermore, 61.9% of the structures had an estimated cube strength that was below the minimum 28-day compressive strength requirement for its environmental conditions, which is particularly concerning given that all of these structures are over 70 years old. As such, it is likely that these structures are at significant risk of deterioration from freeze-thaw attack as well as both carbonation and chloride induced corrosion.

6 HISTORIC SAMPLE STUDY

6.1 INTRODUCTION

The aim of the historic sample study was to analyse a wide variety of cement, mortar and concrete samples from historic structures (pre-dating 1950) across Scotland to determine the differences in Portland cement and other constituents that exist as a result of changes in manufacturing technology and processes over time, available raw materials, and the introduction of material standards and design legislation.

However, there were significant difficulties in obtaining samples, due to the destructive testing requirements and legislation which prevents the removal of material from historically significant structures – as discussed in Chapter 4.2. As such, only 85 samples were obtained – an inventory of which can be found in Chapter 3.2 – and not all of these samples were appropriate for inclusion in the study as they were not Portland cement-based materials or were of indeterminate origin.

Furthermore, complications arose, not only in the range of tests that could be carried out on each sample, but also in the analysis and comparison of tests results due to variations between samples such as size, shape and type (drill cuttings, cored or mass sample). Furthermore, in many cases, the samples were supplied with very little or no supplementary data to aid in the determination of the age of each sample, or even the location from which it was taken. However, when adequate information regarding the structure was provided, its age and approximate grid reference could generally be determined by cross-referencing against the Historic Environment Scotland CANMORE database (https://canmore.org.uk).

6.2 METHODOLOGY

While the general test methodologies used in this study were discussed in Chapter 3.3, the specific calculations and additional steps taken that were not defined in the relevant test standards will be detailed at this stage.

6.2.1 Chemical Composition

The bulk chemical composition of the concrete was determined using XRF spectrometry, as described in Chapter 3.3.4. However, this only supplied the chemical composition of the overall concrete powder sample – not the aggregate or binder individually. As such, the chemical composition of the aggregate had to be determined separately by first completing an XRF analysis of the insoluble reside obtained by acid digestion as described in Chapter 3.3.2.

Once the chemical composition of the insoluble residue had been determined, this then had to be factored by the insoluble residue content of the concrete in order to calculate the actual chemical composition of the insoluble residue as a function of the overall concrete sample:

$$O_{n.ir} = O_{n.IR} \times \frac{IR.}{100} \tag{44}$$

where:

- IR. is the insoluble residue content of the concrete as a percentage;
- $O_{n.ir}$ is the percentage of any given oxide of the insoluble residue as found in the overall concrete sample;
- $O_{n.IR}$ is the normalised percentage of any given oxide of the insoluble residue, as determined by XRF spectrometry.

However, the chemical composition of the insoluble residue is not necessarily representative of the composition of the aggregate, as the insoluble residue inevitably contains amorphous material which is more likely to be a constituent of the cement and not the aggregate – an issue which will be discussed further in Chapter 6.3.2. As such, the chemical composition of the amorphous material had to be calculated and removed from the insoluble residue composition to determine the aggregate composition.

This was carried out in several steps. First, an XRD analysis of the insoluble residue had to be carried out to determine the mineralogical composition of the crystalline phases, and this then had to be converted into an elemental composition. Next, the chemical

composition determined from the XRF of insoluble residue was also converted into an elemental composition, and the previously calculated elemental composition of the crystalline phases subtracted from it to give the elemental composition of the amorphous phases. Finally, the chemical composition of the amorphous phases could be calculated by converting this elemental composition into their associated oxides. However, it should be noted that this method does not take into account trace elements, usually leading to a shortfall in total constituents.

Once the chemical composition of the amorphous material had been calculated, the actual aggregate composition could then be calculated by subtracting the corrected composition of the amorphous material from the insoluble residue:

$$O_{n.a} = O_{n.ir} - \left(O_{n.AM} \times \frac{Am.}{100} \times \frac{IR.}{100}\right) \quad (45)$$

where:

- $O_{n.a}$ is the percentage of any given oxide of the aggregate as found in the overall concrete sample;
- $O_{n.AM}$ is the normalised percentage of any given oxide of the amorphous phases;
- Am. is the percentage sum of the amorphous phases of the insoluble residue.

Finally, the chemical composition of the binder could then be calculated by subtracting the composition of the aggregate from the previously determined chemical composition of the concrete sample:

$$O_{n.b} = O_{n.c} - O_{n.a} \quad (46)$$

where:

- $O_{n.b}$ is the percentage of any given oxide of the binder as found in the overall concrete sample;
- $O_{n.c}$ is the normalised percentage of any given oxide of the total concrete as determined by XRF spectrometry.

6.2.2 Aggregate Content

Determination of aggregate content using the insoluble residue method detailed in BS 1881-124 (British Standards Institution, 2015a) was discussed in Chapter 3.3.2. However, this method assumes two things: Firstly, that the insoluble residue was aggregate only – as per BS 1881-124 (British Standards Institution, 2015a) – and, secondly, that none of the aggregate was acid soluble. However, it is possible that either of these assumptions may be incorrect when this method is applied to any given sample.

In the case of acid soluble aggregate, this can be taken into consideration by performing a point-counting analysis on a thin section of the sample and correcting the results accordingly. It should be noted though, that the thin section analysis of concrete samples presents its own complications which will be discussed further in Chapter 6.3.3.

With regards to insoluble residue being aggregate only, it became clear from the initial chemical analysis of the samples that this was not the case. It was determined that the insoluble residue contained significant amounts of amorphous material which was not acid soluble, but most likely originated from the cement and not the aggregate, as discussed in Chapter 6.2.1.

As such, the aggregate content was calculated by calculating the sum of the bulk oxides for each sample as detailed in Chapter 6.2.1.

$$AC. = \sum O_{n.b} \tag{47}$$

where:

- $O_{n.b}$ is the percentage of each oxide of the binder as found in the overall concrete sample;
- AC. is the aggregate content of the overall concrete sample.

6.3 RESULTS

6.3.1 LOI, Insoluble Residue, Aggregate, Binder & Anhydrous Cement Contents

Table 6-1 – LOI, insoluble residue, aggregate, binder and anhydrous cement contents, part 1 of 3

Sample	Insoluble Residue %	Aggregate Content %	Binder Content %	Loss On Ignition %	Anhydrous Cement %	Normalised LOI %
01	–	55.8	44.2	18.5	25.7	41.9
02	–	–	–	–	–	–
03	70.9	32.7	67.3	6.5	60.8	9.7
04	80.2	45.8	54.2	5.6	48.6	10.4
05	67.9	34.6	65.4	7.5	57.9	11.4
06	72.1	37.7	62.3	7.3	55.0	11.7
07	73.5	42.7	57.3	7.1	50.2	12.4
08	69.4	43.8	56.2	8.1	48.1	14.5
09	60.5	29.4	70.6	9.7	60.9	13.7
10	64.7	34.3	65.7	11.9	53.8	18.1
11	68.0	59.0	41.0	8.8	32.1	21.6
12	65.3	48.3	51.7	9.4	42.3	18.2
13	56.2	21.8	78.2	16.1	62.1	20.6
14	46.0	41.6	58.4	17.5	40.9	29.9
15	74.5	47.5	52.5	6.1	46.4	11.7
16	71.2	52.8	47.2	8.1	39.1	17.1
17	70.4	51.1	48.9	8.9	39.9	18.3
18	70.1	30.6	69.4	8.6	60.7	12.5
19	44.2	22.6	77.4	14.8	62.6	19.1
20	74.4	34.4	65.6	6.9	58.7	10.5
21	82.2	56.8	43.2	3.9	39.3	9.1
22	50.0	31.7	68.3	13.8	54.5	20.2
23	64.0	39.6	60.4	15.5	44.9	25.7
24	68.5	52.5	47.5	12.6	34.9	26.5
25	70.2	33.2	66.8	10.2	56.6	15.3
26	70.0	49.3	50.7	9.7	41.0	19.1
27	–	–	–	–	–	–
28	–	–	–	–	–	–
29	56.3	15.3	84.7	8.3	76.4	9.8
30	57.8	32.5	67.5	10.8	56.8	15.9
31	77.0	33.8	66.2	8.2	58.0	12.4
32	57.5	54.4	45.6	13.7	31.9	30.1
33	59.9	56.6	43.4	13.0	30.4	29.9
34	85.8	44.3	55.7	9.0	46.8	16.1
35	72.2	37.6	62.4	9.6	52.8	15.4

Table 6-2 – LOI, insoluble residue, aggregate, binder and anhydrous cement contents, part 2 of 3

Sample	Insoluble Residue %	Aggregate Content %	Binder Content %	Loss On Ignition %	Anhydrous Cement %	Normalised LOI %
36	13.6	0.1	99.9	35.4	64.5	35.4
37	71.0	31.2	68.8	6.3	62.5	9.1
38	74.6	31.3	68.7	7.7	61.0	11.2
39	55.3	30.1	69.9	9.1	60.8	13.0
40	77.2	59.1	40.9	8.4	32.5	20.5
41	86.1	49.0	51.0	7.4	43.6	14.6
42	–	–	–	–	–	–
43	54.4	3.9	96.1	12.6	83.5	13.1
44	79.8	26.1	73.9	5.7	68.3	7.7
45	81.2	24.0	76.0	5.4	70.6	7.1
46	84.5	41.5	58.5	9.8	48.7	16.8
47	83.8	29.1	70.9	9.0	61.9	12.7
48	70.2	26.6	73.4	7.5	65.9	10.2
49	83.9	42.9	57.1	9.0	48.1	15.7
50	63.5	39.0	61.0	10.5	50.5	17.2
51	46.2	37.0	63.0	17.6	45.4	28.0
52	41.9	25.7	74.3	21.8	52.5	29.3
53	–	–	–	–	–	–
54	–	–	–	–	–	–
55	–	–	–	–	–	–
56	76.6	65.9	34.1	6.9	27.2	20.2
57	72.5	51.0	49.0	9.3	39.7	19.0
58	71.9	44.2	55.8	7.7	48.1	13.8
59	66.0	23.9	76.1	8.1	68.0	10.6
60	9.8	3.6	96.4	29.0	67.3	30.1
61	24.9	14.6	85.4	20.5	64.9	24.0
62	69.5	40.4	59.6	10.4	49.2	17.5
63	66.7	40.4	59.6	13.2	46.4	22.1
64	33.6	17.2	82.8	25.9	56.8	31.3
65	59.6	28.6	71.4	15.9	55.4	22.3
66	53.6	33.2	66.8	13.2	53.6	19.8
67	39.5	36.5	63.5	19.5	44.0	30.7
68	64.2	30.3	69.7	10.8	58.9	15.5
69	75.6	55.0	45.0	10.7	34.3	23.8
70	48.2	46.4	53.6	10.9	42.7	20.4
71	52.7	50.4	49.6	16.8	32.8	33.9
72	61.4	59.4	40.6	13.1	27.5	32.2
73	57.2	26.2	73.8	12.3	61.5	16.7

Table 6-3 – LOI, insoluble residue, aggregate, binder and anhydrous cement contents, part 3 of 3

Sample	Insoluble Residue %	Aggregate Content %	Binder Content %	Loss On Ignition %	Anhydrous Cement %	Normalised LOI %
74	68.7	64.3	35.7	7.8	27.9	21.7
75	97.9	32.6	67.4	1.1	66.3	1.6
76	64.9	58.7	41.3	12.5	28.8	30.3
77	63.9	38.9	61.1	14.5	46.7	23.7
78	56.8	29.2	70.8	15.0	55.8	21.1
79	75.7	38.5	61.5	8.3	53.2	13.5
80	12.5	6.7	93.3	30.0	63.3	32.2
81	–	–	–	–	–	–
82	–	–	–	–	–	–
83	–	–	–	–	–	–
84	76.8	21.8	78.2	4.4	73.8	5.7
85	52.4	26.2	73.8	13.1	60.7	17.8

6.3.1.1 Discussion

With regards to determining aggregate content, as discussed in Chapter 6.2.2, it has been assumed that the amorphous material, most probably present as glassy material, in the concrete is attributed to the cementitious material – not the aggregate. The presence of this glass in clinker is inevitable and while it adversely affects the grindability of clinker it is, to some extent, desirable, as cooling rates which result in its formation also have advantageous effects on the formation of certain clinker constituents (Neville, 2011).

Research carried out by Lerch (1938) approximated the glass contents of Portland cement clinker from 21 plants in the USA using the heat of solution method, and found that they varied from 2 to 21 percent. Furthermore, it was concluded that, for any given clinker composition, the glass content was dependent on the cooling conditions that the clinker was subjected to – with relatively high glass contents caused by cooling the clinker rapidly, and relatively low glass contents by cooling slowly. Strict control of clinker is cooling is essential to ensure the desired degree of crystallisation and glass formation (Neville, 2011).

This presents a problem when dealing with early Portland cements, since the cement manufacturing process was, at that time, very much a process of trial and error – as discussed in Chapter 2.1.3.3 – which made use of varying sources of available raw materials and lacked the modern technology that is used to maintain strict control of the clinkering and cooling processes. As such, it is likely that the glass content of early Portland cements could have varied greatly, not only between manufacturing plants – as shown by Lerch (1938) – but also between batches from the same plant, and this makes it difficult to predict reasonable results for the insoluble amorphous content of cements from historic concrete samples. As it is possible that some aggregates also contain amorphous material, this presents a source of error in the calculation of aggregate and binder contents, and subsequently results in errors in the determination of both aggregate and binder chemical composition.

However, while it is not possible to determine the amount of amorphous material which originates from either the cement or aggregate without original samples of either, the results of the chemical analysis can be examined to determine whether it is likely that the assumption that the amorphous material originates exclusively from the cement is correct. This will be discussed further in discussion of the chemical composition results in Chapter 6.3.2.4.

While it had been hoped that it would be possible to relate cement and aggregate contents in concrete structures throughout Scotland to their date, architectural type, production source, and physical characteristics, there were too few samples obtained for the study to do this with any accuracy. The samples that were obtained were from far too few locations across Scotland, and consisted of too many different types of material – such as varying types of concrete which were cast *in-situ* (reinforced, mass, lightweight), precast concrete, mortar and render.

However, with regards to current forensic analysis techniques, it can be concluded that comparing the insoluble residue and aggregate contents obtained shows a clear and significant difference between these values, which suggests that the use of insoluble residue content only as a means of determining aggregate content of historic concrete is likely to be extremely unreliable and inaccurate. Furthermore, the use of incorrect aggregate content values will subsequently result in incorrect determinations of chemical composition of both aggregate and binder.

6.3.2 Chemical Composition

6.3.2.1 Concrete

Table 6-4 – Normalised chemical composition of concrete samples, part 1 of 5 (samples 01-17)

	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17
Al_2O_3	3.1	-	14.7	16.9	15.1	16.6	16.7	14.6	14.1	14.8	15.1	15.8	10.1	9.3	10.7	10.7	10.4
CaO	39.1	-	19.1	10.7	20.9	17.3	15.1	16.7	24.5	21.4	18.1	21.9	27.0	32.4	9.0	13.9	15.4
Cl	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Fe_2O_3	1.4	-	6.0	7.0	6.7	6.2	6.2	6.1	6.2	7.0	5.5	6.7	11.0	10.6	7.4	10.1	9.0
K_2O	0.0	-	3.2	3.9	3.4	4.2	4.1	3.3	3.3	3.4	3.6	3.4	0.8	0.7	1.9	1.2	1.2
MgO	0.5	-	2.3	2.7	2.3	2.3	2.2	2.2	2.1	2.1	1.9	2.2	7.1	6.2	2.7	3.3	3.1
MnO	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.1	0.1	0.1
Na_2O	0.2	-	1.0	1.2	1.0	1.2	1.2	1.4	1.2	1.7	1.0	1.0	1.4	1.2	2.5	1.9	1.5
P_2O_5	0.2	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.4	0.4	0.4	0.5	0.4
SiO_2	55.0	-	52.3	56.3	48.9	50.4	52.9	54.2	46.8	48.2	53.3	47.3	40.1	36.3	63.8	56.2	56.8
SO_3	0.6	-	0.7	0.3	0.8	0.6	0.5	0.7	0.8	0.4	0.7	0.8	0.6	1.0	0.6	0.5	0.5
Sr	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
TiO_2	0.0	-	0.7	0.8	0.7	1.1	1.1	0.7	0.9	0.8	0.7	0.8	1.5	1.6	0.9	1.7	1.3
Sum	*100*	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-5 – Normalised chemical composition of concrete samples, part 2 of 5 (samples 18-34)

	18	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**
Al_2O_3	10.8	6.9	12.7	8.7	10.6	9.9	9.5	3.6	8.5	-	-	9.9	7.3	6.9	6.7	7.0	8.5
CaO	15.5	39.4	15.5	11.5	31.4	23.1	24.8	29.1	19.8	-	-	30.1	35.6	19.6	40.8	29.4	19.8
Cl	0.0	0.6	0.0	1.1	0.3	0.0	0.0	0.1	0.1	-	-	0.3	0.1	0.0	0.3	0.0	0.1
Fe_2O_3	10.1	4.2	3.5	2.9	5.8	5.1	5.3	1.6	7.9	-	-	4.8	3.4	2.3	4.1	5.1	3.5
K_2O	1.2	0.9	2.2	0.8	1.2	1.9	1.1	0.1	1.0	-	-	1.0	1.2	1.6	1.0	1.2	1.7
MgO	3.9	2.3	2.0	0.9	2.3	2.8	1.2	1.4	2.0	-	-	1.9	1.3	1.2	1.2	1.3	2.3
MnO	0.2	0.0	0.0	0.1	0.7	0.1	0.1	0.1	0.1	-	-	0.1	0.1	0.0	0.1	0.1	0.1
Na_2O	1.7	0.5	2.6	0.6	0.4	0.6	0.5	0.1	1.5	-	-	1.3	0.7	0.8	0.5	0.6	1.0
P_2O_5	0.5	0.3	0.2	0.1	0.3	0.2	0.3	0.1	0.3	-	-	0.3	0.2	0.2	0.2	0.2	0.2
SiO_2	53.9	41.9	60.1	72.4	44.9	55.5	55.8	61.9	56.6	-	-	48.1	48.1	66.3	43.0	53.9	61.2
SO_3	0.5	2.4	0.6	0.6	1.6	0.2	0.8	1.7	1.3	-	-	1.4	1.6	0.7	1.5	0.9	1.0
Sr	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	-	-	0.0	0.0	0.0	0.0	0.0	0.0
TiO_2	1.6	0.5	0.6	0.3	0.6	0.6	0.6	0.2	0.8	-	-	0.7	0.4	0.4	0.5	0.4	0.4
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	-	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-6 – Normalised chemical composition of concrete samples, part 3 of 5 (samples 35-51)

	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
Al_2O_3	9.2	5.8	11.2	9.1	7.7	8.1	8.1	-	19.0	16.2	17.7	11.3	11.4	12.3	7.6	9.7	7.4
CaO	14.9	62.9	19.2	15.3	37.6	18.2	14.5	-	22.8	16.8	16.5	23.4	23.2	17.6	33.2	25.5	35.7
Cl	0.0	0.4	0.2	0.6	0.9	0.0	0.0	-	0.4	0.2	0.3	0.0	0.0	0.1	0.0	0.1	0.4
Fe_2O_3	3.9	3.3	6.0	6.3	2.6	2.9	2.9	-	7.0	12.1	10.8	5.9	5.5	6.0	3.9	3.4	3.3
K_2O	1.5	0.5	1.4	0.9	0.9	1.7	1.8	-	1.6	0.3	0.5	1.1	1.3	1.3	0.5	0.9	0.8
MgO	1.8	1.7	2.5	1.6	1.2	1.6	1.6	-	1.9	6.1	5.2	2.9	2.7	3.5	1.0	1.3	1.2
MnO	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Na_2O	1.8	0.7	2.0	1.5	0.5	1.0	1.1	-	0.5	1.7	1.7	1.8	1.8	2.0	0.3	0.5	0.7
P_2O_5	0.3	0.2	0.4	0.3	0.2	0.3	0.2	-	0.2	0.1	0.1	0.3	0.3	0.3	0.2	0.3	0.2
SiO_2	65.5	22.8	55.0	62.9	45.9	64.8	68.5	-	43.7	44.2	44.9	51.3	51.9	54.8	51.3	56.2	47.5
SO_3	0.5	1.5	1.0	0.8	2.2	1.0	0.9	-	1.8	0.4	0.5	1.0	1.0	1.1	1.3	1.5	2.3
Sr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.1
TiO_2	0.5	0.4	1.0	0.6	0.4	0.4	0.4	-	0.8	1.7	1.6	0.9	0.7	0.9	0.4	0.6	0.4
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-7 – Normalised chemical composition of concrete samples, part 4 of 5 (samples 52-68)

	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68
Al_2O_3	6.9	-	-	-	13.2	13.1	12.6	11.7	5.5	6.2	6.1	3.9	3.5	8.5	7.0	8.4	7.2
CaO	39.7	-	-	-	14.3	17.1	17.5	22.0	63.8	57.7	21.7	25.9	50.6	26.4	30.6	38.0	26.6
Cl	0.4	-	-	-	0.0	0.0	0.0	0.5	1.0	0.7	0.4	0.1	0.0	0.0	0.0	0.6	0.1
Fe_2O_3	3.5	-	-	-	4.4	3.5	3.9	3.8	2.6	2.9	2.2	1.7	3.1	3.7	2.8	4.9	2.9
K_2O	0.7	-	-	-	2.1	2.2	2.0	1.6	0.3	0.2	1.3	0.7	0.4	1.6	1.1	0.7	1.2
MgO	1.2	-	-	-	0.0	2.1	2.1	1.7	1.8	2.0	1.3	1.0	1.7	2.8	1.6	3.2	1.5
MnO	0.1	-	-	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Na_2O	0.7	-	-	-	2.5	2.4	2.1	1.8	0.4	0.6	0.6	0.4	0.4	1.2	0.8	0.9	0.7
P_2O_5	0.2	-	-	-	0.2	0.2	0.2	0.2	0.3	0.1	0.2	0.2	0.3	0.2	0.2	0.4	0.2
SiO_2	43.4	-	-	-	62.5	58.6	58.0	55.3	21.4	27.4	64.1	63.3	38.1	54.2	54.0	40.4	57.6
SO_3	2.5	-	-	-	0.4	0.4	1.0	1.0	2.4	1.7	1.7	2.4	1.5	0.9	1.4	2.1	1.5
Sr	0.1	-	-	-	0.0	0.0	0.0	0.0	0.3	0.1	0.0	0.0	0.3	0.0	0.0	0.0	0.0
TiO_2	0.5	-	-	-	0.5	0.4	0.4	0.4	0.3	0.2	0.4	0.2	0.3	0.4	0.4	0.6	0.4
Sum	*100*	-	-	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-8 – Normalised chemical composition of concrete samples, part 5 of 5 (samples 69-85)

	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85
Al_2O_3	13.4	6.6	7.7	4.1	11.0	9.4	6.9	8.5	8.4	8.4	10.9	4.6	-	-	-	14.1	10.1
CaO	15.6	38.9	30.1	30.1	24.2	21.9	0.2	22.4	25.3	29.8	15.5	65.7	-	-	-	15.1	31.9
Cl	0.0	0.1	0.0	0.1	0.0	0.5	0.0	0.3	0.1	2.5	0.1	1.8	-	-	-	0.0	0.1
Fe_2O_3	1.6	2.6	3.5	2.2	8.4	6.9	1.2	3.0	3.5	3.5	3.2	2.4	-	-	-	12.0	5.8
K_2O	3.7	1.0	1.4	0.5	1.1	0.8	0.0	2.5	2.3	1.9	2.6	0.4	-	-	-	0.7	2.8
MgO	0.6	1.4	4.4	1.0	4.1	2.5	0.0	2.3	2.9	2.6	1.3	1.6	-	-	-	6.3	1.8
MnO	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	-	-	-	0.2	0.1
Na_2O	2.3	0.6	1.0	0.2	2.1	1.3	0.0	1.1	1.0	0.7	0.7	0.3	-	-	-	1.8	1.6
P_2O_5	0.1	0.2	0.2	0.2	0.4	0.3	0.0	0.2	0.3	0.2	0.2	0.2	-	-	-	0.3	0.3
SiO_2	61.8	45.5	50.1	59.4	45.4	54.4	91.7	58.7	54.9	48.1	64.3	21.0	-	-	-	46.7	42.0
SO_3	0.6	2.7	1.1	1.9	2.1	1.1	0.0	0.6	0.8	1.7	0.8	1.5	-	-	-	0.6	3.2
Sr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.2	-	-	-	0.1	0.1
TiO_2	0.2	0.4	0.5	0.3	1.1	1.0	0.0	0.4	0.5	0.4	0.4	0.3	-	-	-	2.1	0.4
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	-	-	*100*	*100*

6.3.2.2 Aggregate

Table 6-9 – Normalised estimation of chemical composition of aggregate, part 1 of 5 (samples 01a-17a)

	01a	02a	03a	04a	05a	06a	07a	08a	09a	10a	11a	12a	13a	14a	15a	16a	17a
Al_2O_3	2.0	-	22.9	15.7	17.3	19.8	19.8	17.5	17.4	16.7	14.1	19.5	7.2	12.4	8.0	8.5	9.4
CaO	0.4	-	0.1	0.1	0.1	0.1	0.0	0.2	0.1	0.5	0.1	0.0	2.0	5.7	1.1	2.2	1.9
Cl	0.0	-	0.3	0.1	0.1	0.1	0.1	0.0	0.1	0.2	0.1	0.1	0.5	0.1	0.1	0.1	0.1
Fe_2O_3	0.8	-	1.6	1.8	1.2	2.2	1.2	2.1	1.2	2.2	1.5	2.2	2.7	6.7	1.9	2.9	2.8
K_2O	0.7	-	6.4	4.2	4.9	5.4	5.8	4.8	5.0	4.4	3.6	5.2	2.5	1.0	1.4	2.4	1.4
MgO	0.1	-	0.7	0.8	0.5	1.0	0.5	0.8	0.5	0.8	0.7	0.9	1.9	4.5	0.7	1.0	1.1
MnO	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.1	0.1	0.1	0.1
Na_2O	0.2	-	0.9	0.9	0.6	1.1	0.6	0.9	0.6	0.8	0.7	0.9	0.8	2.0	2.2	1.5	1.5
P_2O_5	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
SiO_2	95.6	-	65.4	74.9	73.5	68.1	70.1	72.5	73.0	72.6	78.2	70.0	76.1	64.8	82.7	78.4	79.1
SO_3	0.1	-	0.1	0.1	0.3	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.8	0.3	0.2	0.4	0.4
Sr	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
TiO_2	0.2	-	1.6	1.4	1.6	2.2	1.9	1.1	2.1	1.6	0.9	1.2	5.2	2.3	1.5	2.5	2.0
Sum	*100*	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-10 – Normalised estimation of chemical composition of aggregate, part 2 of 5 (samples 18a-34a)

	18a	19a	20a	21a	22a	23a	24a	25a	26a	27a	28a	29a	30a	31a	32a	33a	34a
Al_2O_3	5.6	2.2	10.1	3.9	5.6	5.6	2.8	0.0	6.6	-	-	9.6	0.1	1.0	5.5	5.2	2.7
CaO	0.8	0.1	0.9	0.3	0.1	0.0	0.1	0.0	1.5	-	-	0.0	-0.1	0.0	0.9	0.4	0.1
Cl	0.3	0.2	0.1	0.1	0.6	0.5	0.3	0.1	0.3	-	-	0.2	0.5	0.1	0.0	0.0	0.1
Fe_2O_3	1.5	0.2	1.8	0.5	0.7	0.3	0.5	0.0	2.8	-	-	0.0	-0.1	0.1	2.2	1.4	0.3
K_2O	1.6	0.9	1.7	1.0	1.8	2.7	0.8	0.0	1.0	-	-	8.9	0.4	0.7	1.1	1.4	1.4
MgO	0.6	0.2	1.2	0.1	0.3	0.2	0.1	0.0	0.7	-	-	0.0	-0.1	0.0	0.6	0.5	0.2
MnO	0.2	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.1	-	-	0.2	0.1	0.0	0.1	0.0	0.1
Na_2O	0.8	0.1	2.2	0.2	0.2	0.1	0.1	0.0	1.1	-	-	0.0	-0.1	0.1	1.1	0.9	0.2
P_2O_5	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	-	-	0.1	0.1	0.0	0.0	0.0	0.0
SiO_2	83.7	94.8	80.7	93.3	89.5	89.4	94.4	99.6	84.4	-	-	78.1	98.3	97.2	87.9	89.8	94.1
SO_3	0.5	0.1	0.1	0.0	0.1	0.1	0.2	0.1	0.1	-	-	0.1	0.1	0.1	0.1	0.0	0.1
Sr	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	-	-	0.2	0.0	0.0	0.0	0.0	0.0
TiO_2	4.1	1.0	1.2	0.4	1.1	1.0	0.7	0.1	1.4	-	-	2.7	0.8	0.7	0.6	0.3	0.8
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	-	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-11 – Normalised estimation of chemical composition of aggregate, part 3 of 5 (samples 35a-51a)

	35a	36a	37a	38a	39a	40a	41a	42a	43a	44a	45a	46a	47a	48a	49a	50a	51a
Al_2O_3	4.8	-2.4	10.4	4.5	3.1	1.4	1.8	-	-6.4	16.2	16.9	11.5	7.8	6.1	0.2	2.6	3.8
CaO	0.4	-0.7	1.6	0.1	0.0	0.1	0.1	-	-0.3	9.3	9.5	2.6	1.6	1.4	0.0	0.0	0.1
Cl	0.2	122.3	0.1	0.2	0.1	0.1	0.3	-	6.2	0.2	0.2	0.2	0.7	0.4	0.4	0.1	0.1
Fe_2O_3	0.7	-0.9	2.4	0.7	0.2	0.2	0.3	-	-1.7	10.3	9.0	2.6	1.7	1.2	0.1	0.2	0.6
K_2O	1.8	-0.3	4.0	1.1	2.4	0.7	0.7	-	-0.5	0.3	0.4	1.5	1.1	0.9	0.0	0.9	1.1
MgO	0.2	-0.3	0.4	0.2	0.1	0.1	0.1	-	-0.3	5.8	4.8	1.0	0.7	0.4	0.0	0.1	0.2
MnO	0.1	1.4	0.2	0.1	0.0	0.0	0.0	-	0.6	0.4	0.4	0.2	0.1	0.2	0.0	0.0	0.0
Na_2O	0.6	-3.4	1.7	0.4	0.1	0.2	0.2	-	-0.2	2.0	1.9	1.8	1.4	1.2	0.0	0.1	0.3
P_2O_5	0.0	1.9	0.1	0.1	0.0	0.0	0.0	-	1.6	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0
SiO_2	90.0	-88.4	76.3	91.0	93.2	96.7	95.8	-	83.8	49.4	49.9	76.6	82.1	85.5	98.1	95.1	93.2
SO_3	0.0	18.7	0.1	0.1	0.1	0.1	0.1	-	3.2	0.5	0.5	0.1	0.1	0.1	0.1	0.1	0.1
Sr	0.0	0.1	0.1	0.0	0.0	0.0	0.0	-	0.4	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0
TiO_2	1.0	52.1	2.6	1.6	0.6	0.4	0.5	-	13.5	5.4	6.2	1.9	2.4	2.4	0.7	0.8	0.5
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-12 – Normalised estimation of chemical composition of aggregate, part 4 of 5 (samples 52a-68a)

	52a	53a	54a	55a	56a	57a	58a	59a	60a	61a	62a	63a	64a	65a	66a	67a	68a
Al_2O_3	2.2	-	-	-	11.8	12.0	11.2	9.6	5.9	6.9	1.3	0.2	0.3	6.0	3.5	8.4	1.6
CaO	0.1	-	-	-	2.9	2.0	2.2	2.1	1.5	1.2	0.0	0.0	0.0	0.1	0.1	1.5	0.1
Cl	0.6	-	-	-	0.0	0.0	0.1	0.1	1.3	0.3	0.1	0.1	0.1	0.4	0.2	0.4	0.1
Fe_2O_3	0.3	-	-	-	1.9	1.0	1.3	1.2	1.1	0.9	0.1	0.0	0.2	1.0	0.4	2.4	0.2
K_2O	0.8	-	-	-	2.1	3.1	2.1	1.8	1.6	3.3	0.9	0.2	0.0	1.6	1.5	2.4	0.9
MgO	0.1	-	-	-	1.6	0.6	1.1	0.5	0.5	0.4	0.1	0.0	0.0	0.5	0.2	1.2	0.1
MnO	0.0	-	-	-	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Na_2O	0.2	-	-	-	2.7	2.6	2.4	2.2	1.2	1.1	0.1	0.0	0.0	0.9	0.3	1.4	0.2
P_2O_5	0.1	-	-	-	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.1	0.2	0.1	0.0	0.0	0.0
SiO_2	94.8	-	-	-	76.5	78.2	79.2	81.6	85.2	85.3	96.8	99.0	98.5	88.5	93.3	81.3	96.1
SO_3	0.2	-	-	-	0.0	0.0	0.1	0.1	0.7	0.1	0.1	0.1	0.2	0.0	0.1	0.1	0.1
Sr	0.0	-	-	-	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TiO_2	0.7	-	-	-	0.3	0.3	0.4	0.6	0.6	0.3	0.5	0.3	0.4	0.9	0.6	0.8	0.7
Sum	*100*	-	-	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-13 – Normalised estimation of chemical composition of aggregate, part 5 of 5 (samples 69a-85a)

	69a	70a	71a	72a	73a	74a	75a	76a	77a	78a	79a	80a	81a	82a	83a	84a	85a
Al_2O_3	11.2	5.4	2.4	1.4	13.0	8.8	4.1	6.3	4.4	4.7	2.0	4.3	-	-	-	11.1	13.7
CaO	0.1	0.3	0.2	0.0	1.8	2.7	0.0	0.0	0.0	0.0	0.0	0.0	-	-	-	5.2	0.9
Cl	0.1	0.1	0.6	0.1	0.5	0.0	0.1	0.0	0.1	0.3	0.2	0.8	-	-	-	2.7	1.3
Fe_2O_3	0.3	0.9	0.3	0.1	1.3	4.2	1.0	0.2	0.2	0.1	0.0	0.3	-	-	-	4.7	3.2
K_2O	4.1	1.7	1.1	1.0	7.6	1.5	0.5	2.7	1.6	2.2	1.1	1.7	-	-	-	3.0	4.1
MgO	0.1	0.3	0.2	0.0	0.4	1.6	0.4	0.2	0.2	0.1	0.0	0.2	-	-	-	2.3	1.0
MnO	0.0	0.0	0.0	0.0	1.3	0.8	0.0	0.1	0.0	0.1	0.0	0.0	-	-	-	0.4	0.6
Na_2O	1.7	0.8	0.4	0.1	0.8	1.5	0.0	0.6	0.4	0.2	0.0	0.4	-	-	-	1.8	1.5
P_2O_5	0.1	0.0	0.0	0.0	0.2	0.3	0.5	0.1	0.2	0.2	0.5	0.1	-	-	-	0.2	0.4
SiO_2	81.8	90.1	94.3	97.0	69.4	77.2	92.6	89.1	92.1	91.0	94.3	91.2	-	-	-	59.6	70.6
SO_3	0.3	0.0	0.0	0.0	1.0	0.1	0.0	0.3	0.2	0.2	1.1	0.2	-	-	-	0.2	1.8
Sr	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-	-	0.2	0.1
TiO_2	0.2	0.3	0.5	0.2	2.5	1.1	0.8	0.4	0.6	0.8	0.6	0.8	-	-	-	8.5	0.8
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	-	-	*100*	*100*

6.3.2.3 Binder

Table 6-14 – Normalised estimation of chemical composition of binder, part 1 of 5 (samples 01b-17b)

	01b	02b	03b	04b	05b	06b	07b	08b	09b	10b	11b	12b	13b	14b	15b	16b	17b
Al_2O_3	5.5	-	10.7	17.9	14.0	14.7	14.4	12.4	12.7	13.9	16.5	12.2	11.0	7.2	13.2	13.2	11.5
CaO	68.3	-	28.3	19.6	32.0	27.7	26.3	29.5	34.7	32.3	44.0	42.4	33.9	51.4	16.1	27.0	29.6
Cl	0.0	-	-0.1	-0.1	0.0	0.0	-0.1	0.0	0.0	-0.1	-0.2	-0.1	-0.1	0.2	-0.1	-0.1	-0.2
Fe_2O_3	2.5	-	8.1	11.3	9.6	8.6	9.8	9.3	8.3	9.5	11.3	10.9	13.3	13.4	12.5	18.1	15.4
K_2O	1.0	-	1.6	3.7	2.5	3.5	2.8	2.1	2.5	2.9	3.5	1.8	0.3	0.4	2.4	-0.2	1.0
MgO	0.8	-	3.0	4.3	3.3	3.1	3.4	3.3	2.8	2.8	3.7	3.4	8.6	7.4	4.4	5.9	5.2
MnO	0.1	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.2	0.1	0.1
Na_2O	0.3	-	1.1	1.6	1.3	1.3	1.7	1.8	1.5	2.1	1.4	1.1	1.6	0.7	2.7	2.3	1.5
P_2O_5	0.3	-	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.4	0.3	0.5	0.7	0.7	0.9	0.8
SiO_2	19.8	-	45.9	40.6	35.9	39.8	40.0	40.0	35.9	35.4	17.3	26.0	30.0	16.0	46.6	31.5	33.4
SO_3	1.1	-	0.9	0.6	1.1	0.9	0.9	1.1	1.0	0.5	1.4	1.4	0.5	1.5	1.0	0.5	0.7
Sr	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	0.2
TiO_2	0.3	-	0.2	0.3	0.2	0.5	0.5	0.3	0.4	0.4	0.6	0.5	0.4	1.0	0.4	0.7	0.6
Sum	*100*	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-15 – Normalised estimation of chemical composition of binder, part 2 of 5 (samples 18b-34b)

	18b	19b	20b	21b	22b	23b	24b	25b	26b	27b	28b	29b	30b	31b	32b	33b	34b
Al_2O_3	13.0	8.2	14.1	14.8	12.9	12.8	16.9	5.5	10.4	-	-	10.0	10.7	9.9	8.1	9.2	13.2
CaO	22.0	50.9	23.2	26.2	45.9	38.3	52.1	43.5	37.7	-	-	35.5	52.7	29.5	88.4	67.4	35.5
Cl	-0.1	0.7	-0.1	2.4	0.2	-0.3	-0.2	0.1	-0.1	-	-	0.3	0.0	0.0	0.6	0.0	0.2
Fe_2O_3	13.9	5.4	4.4	6.0	8.1	8.3	10.6	2.3	12.9	-	-	5.7	5.0	3.4	6.3	9.9	6.1
K_2O	1.0	0.9	2.5	0.6	0.9	1.4	1.5	0.2	1.0	-	-	-0.5	1.6	2.1	0.9	0.8	1.9
MgO	5.3	2.9	2.5	2.0	3.2	4.5	2.5	2.1	3.3	-	-	2.2	2.0	1.9	1.9	2.4	3.9
MnO	0.1	0.0	0.0	0.1	1.0	0.1	0.2	0.1	0.1	-	-	0.1	0.0	0.1	0.1	0.1	0.1
Na_2O	2.1	0.6	2.8	1.2	0.5	0.9	1.0	0.1	1.8	-	-	1.6	1.1	1.1	-0.1	0.2	1.7
P_2O_5	0.6	0.4	0.3	0.3	0.4	0.3	0.5	0.2	0.5	-	-	0.3	0.3	0.3	0.5	0.4	0.4
SiO_2	40.8	26.4	49.3	44.8	24.2	33.2	13.0	43.2	29.6	-	-	42.7	24.0	50.5	-10.4	7.0	35.2
SO_3	0.5	3.1	0.8	1.4	2.3	0.3	1.5	2.5	2.5	-	-	1.7	2.3	1.0	3.2	2.0	1.7
Sr	0.2	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	-	-	0.0	0.0	0.0	0.0	0.0	0.0
TiO_2	0.5	0.4	0.2	0.2	0.3	0.3	0.4	0.2	0.3	-	-	0.3	0.3	0.2	0.4	0.5	0.2
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	-	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-16 – Normalised estimation of chemical composition of binder, part 3 of 5 (samples 35b-51b)

	35b	36b	37b	38b	39b	40b	41b	42b	43b	44b	45b	46b	47b	48b	49b	50b	51b
Al_2O_3	11.8	5.8	11.5	11.2	9.6	17.9	14.0	-	20.1	16.2	18.0	11.1	12.9	14.6	13.1	14.2	9.5
CaO	23.7	62.9	27.2	22.2	53.7	44.5	28.4	-	23.8	19.4	18.7	38.0	32.1	23.5	58.1	41.8	56.6
Cl	-0.1	0.2	0.3	0.8	1.2	-0.2	-0.3	-	0.2	0.2	0.3	-0.1	-0.3	0.0	-0.2	0.2	0.5
Fe_2O_3	5.8	3.3	7.7	8.9	3.7	6.7	5.4	-	7.4	12.8	11.4	8.3	7.1	7.8	6.8	5.5	4.9
K_2O	1.3	0.5	0.2	0.8	0.3	3.1	2.8	-	1.7	0.3	0.5	0.9	1.3	1.5	0.8	0.9	0.6
MgO	2.8	1.7	3.4	2.2	1.6	3.7	3.0	-	2.0	6.2	5.3	4.2	3.5	4.6	1.8	2.1	1.9
MnO	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1
Na_2O	2.4	0.7	2.1	2.0	0.7	2.2	1.9	-	0.5	1.5	1.6	1.8	2.0	2.3	0.6	0.8	0.9
P_2O_5	0.5	0.2	0.6	0.4	0.2	0.6	0.4	-	0.1	0.1	0.1	0.4	0.3	0.3	0.3	0.4	0.3
SiO_2	50.7	22.9	45.3	50.0	25.5	18.6	42.4	-	42.1	42.4	43.3	33.4	39.5	43.7	16.2	31.4	20.8
SO_3	0.8	1.4	1.4	1.1	3.1	2.2	1.7	-	1.7	0.4	0.5	1.7	1.3	1.4	2.2	2.3	3.5
Sr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	-0.1	0.1	0.1	0.1	0.1	0.1
TiO_2	0.2	0.3	0.3	0.2	0.3	0.4	0.2	-	0.3	0.3	0.2	0.2	0.0	0.3	0.3	0.4	0.4
Sum	*100*	*100*	*100*	*33.3*	*100*	*100*	*100*	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-17 – Normalised estimation of chemical composition of binder, part 4 of 5 (samples 52b-68b)

	52b	53b	54b	55b	56b	57b	58b	59b	60b	61b	62b	63b	64b	65b	66b	67b	68b
Al_2O_3	8.6	-	-	-	15.9	14.2	13.8	12.4	5.5	6.1	9.4	6.3	4.2	9.5	8.7	8.4	9.7
CaO	53.4	-	-	-	36.3	32.8	29.6	28.2	66.2	67.4	36.4	43.5	61.1	37.0	45.9	58.9	38.1
Cl	0.3	-	-	-	-0.1	0.0	-0.1	0.6	1.0	0.8	0.6	0.2	0.0	-0.2	-0.1	0.8	0.1
Fe_2O_3	4.6	-	-	-	9.0	6.1	6.0	4.6	2.7	3.2	3.7	2.9	3.7	4.7	4.0	6.3	4.0
K_2O	0.7	-	-	-	2.0	1.4	2.0	1.5	0.2	-0.3	1.6	1.1	0.5	1.6	0.9	-0.2	1.4
MgO	1.6	-	-	-	-3.1	3.7	3.0	2.1	1.8	2.2	2.1	1.7	2.0	3.7	2.3	4.3	2.1
MnO	0.1	-	-	-	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
Na_2O	0.9	-	-	-	2.2	2.2	1.9	1.7	0.3	0.5	0.9	0.6	0.5	1.4	1.1	0.5	1.0
P_2O_5	0.2	-	-	-	0.7	0.5	0.4	0.3	0.3	0.1	0.4	0.4	0.3	0.3	0.3	0.5	0.3
SiO_2	25.7	-	-	-	35.4	38.3	41.3	47.1	19.0	17.5	42.0	39.2	25.5	40.5	34.5	16.9	40.9
SO_3	3.3	-	-	-	1.0	0.7	1.7	1.3	2.5	2.0	2.7	3.9	1.8	1.2	2.1	3.2	2.1
Sr	0.1	-	-	-	-0.1	-0.1	-0.1	0.0	0.3	0.1	0.0	0.0	0.3	0.0	0.0	0.0	0.0
TiO_2	0.5	-	-	-	0.8	0.4	0.3	0.3	0.2	0.2	0.3	0.2	0.2	0.2	0.3	0.5	0.2
Sum	*100*	-	-	-	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*

Table 6-18 – Normalised estimation of chemical composition of binder, part 5 of 5 (samples 69b-85b)

	69b	70b	71b	72b	73b	74b	75b	76b	77b	78b	79b	80b	81b	82b	83b	84b	85b
Al_2O_3	16.1	7.8	13.2	8.2	10.3	10.4	8.2	11.8	10.9	9.9	16.4	4.6	-	-	-	15.0	8.8
CaO	34.4	72.3	60.5	74.0	32.1	56.4	0.3	54.1	41.4	42.1	25.1	70.4	-	-	-	17.9	43.0
Cl	-0.1	0.2	-0.6	0.3	-0.2	1.2	0.0	0.8	0.1	3.5	0.1	1.9	-	-	-	-0.7	-0.4
Fe_2O_3	3.1	4.0	6.7	5.1	11.0	11.7	1.3	7.1	5.6	4.9	5.1	2.5	-	-	-	14.0	6.7
K_2O	3.3	0.4	1.8	-0.3	-1.2	-0.4	-0.2	2.2	2.7	1.8	3.6	0.3	-	-	-	0.1	2.3
MgO	1.2	2.2	8.7	2.4	5.4	4.0	-0.2	5.2	4.6	3.6	2.1	1.7	-	-	-	7.4	2.0
MnO	0.2	0.0	0.0	0.0	-0.4	-1.4	0.0	0.0	0.1	0.0	0.1	0.1	-	-	-	0.1	-0.2
Na_2O	2.9	0.4	1.6	0.5	2.6	0.7	0.0	1.9	1.5	0.9	1.1	0.3	-	-	-	1.8	1.6
P_2O_5	0.2	0.4	0.5	0.4	0.5	0.4	-0.2	0.3	0.3	0.2	0.0	0.2	-	-	-	0.4	0.2
SiO_2	37.5	6.9	5.1	4.3	36.9	13.4	91.3	15.4	31.3	30.5	45.5	16.0	-	-	-	43.1	31.8
SO_3	1.0	5.0	2.2	4.6	2.5	2.9	0.0	0.9	1.1	2.4	0.6	1.5	-	-	-	0.7	3.7
Sr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.2	-	-	-	0.0	0.1
TiO_2	0.3	0.4	0.4	0.4	0.6	0.6	-0.4	0.4	0.3	0.3	0.2	0.2	-	-	-	0.2	0.3
Sum	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	-	-	-	*100*	*100*

6.3.2.4 Discussion

Errors in Chemical Analysis

The chemical analysis of the powdered concrete samples was complicated by the inability to directly analyse either the binder or aggregate. Instead, the chemical composition of the concrete had to be analysed by XRF and the insoluble residue by both XRD and XRF, and the composition of the aggregate and binder estimated from these results – as described in Chapter 6.2.

As discussed in Chapter 6.3.1.1, this method was further complicated by the presence of amorphous 'glass' from the cement, which is also insoluble. As such, this introduced a significant source of error – not only through the possibly incorrect assumption that all insoluble residue was attributed to the cement, but also through the compounding of experimental error inherent to each XRF and XRD analysis. This error is then magnified when the chemical composition is normalised, as shown in the previous tables in Chapters 6.3.2.1, 6.3.2.2 and 6.3.2.3.

However, it is only possible to positively identify errors in the analyses when they result in a negative estimation of chemical composition. While the majority of these negative results are relatively minor (less than 1%), there are four instances, summarised in Table 6-19, in which more significant errors can be observed.

Table 6-19 – Chemical compositions with significant observed errors

	36a	**43a**	**32b**	**56b**
Al_2O_3	-2.4	-6.4	8.1	15.9
CaO	-0.7	-0.3	88.4	36.3
Cl	122.3	6.2	0.6	-0.1
Fe_2O_3	-0.9	-1.7	6.3	9.0
K2O	-0.3	-0.5	0.9	2.0
MgO	-0.3	-0.3	1.9	-3.1
MnO	1.4	0.6	0.1	-0.1
Na_2O	-3.4	-0.2	-0.1	2.2
P_2O_5	1.9	1.6	0.5	0.7
SiO_2	-88.4	83.8	-10.4	35.4
SO_3	18.7	3.2	3.2	1.0
Sr	0.1	0.4	0.0	-0.1
TiO_2	52.1	13.5	0.4	0.8
Sum	*100*	*100*	*100*	*100*

As previously discussed, it has been assumed that all the amorphous material should be attributed to the cement and not the aggregate, but, in reality, this may be incorrect. This is likely to be the case with sample 43, as it was found to contain artificial lightweight aggregate, as shown in Figure 6-1, and it is probable that this aggregate contained a significant amount of amorphous material. At this stage, it is not possible to determine the proportion of amorphous material that should be attributed to either the cement or the aggregate. However, Table 6-20 shows the variations in composition when 100% of the amorphous material is attributed to either the cement or aggregate. In reality, the true composition probably lies somewhere in the broad range between these two results.

Figure 6-1 – Photograph of sample 43 (left) and sample 36 (right)

Table 6-20 – Two possible chemical compositions of aggregate from sample 43

	AMORPHOUS ATTRIBUTED TO BINDER	AMORPHOUS ATTRIBUTED TO AGGREGATE	DIFFERENCE
Al_2O_3	-6.4	27.1	33.5
CaO	-0.3	1.4	1.7
Cl	6.2	0.4	5.8
Fe_2O_3	-1.7	7.1	8.8
K_2O	-0.5	2.1	2.6
MgO	-0.3	1.4	1.7
MnO	0.6	0.0	0.6
Na_2O	-0.2	0.7	0.9
P_2O5	1.6	0.1	1.5
SiO_2	83.8	58.4	25.4
SO_3	3.2	0.2	3.0
Sr	0.4	0.0	0.4
TiO_2	13.5	1.0	12.5
Sum	*100*	*100*	–

The most significant of the errors found in aggregate composition are in the results of those from sample 36. However, these can be explained in a similar way by examining the aggregate content results found in Table 6-2. Sample 36 was a foamed concrete which had an aggregate content of only 0.1%, and so it can be concluded that, while there are inevitably some errors inherent to the results, the extent of these has been significantly exaggerated as a result of normalisation.

Similarly, it can be hypothesised that the magnitude of the errors encountered in the binder composition of both sample 32 and 56 are a result of small experimental errors which are exaggerated when the composition is normalised. This can be confirmed by examining the differences between the normalised chemical composition and the chemical composition as a proportion of the actual concrete sample, as shown in Table 6-21.

While this reveals a relatively small actual error of -1.0% in the MgO content of sample 56b, sample 32b shows an error of 4.8%, which is unusually high to be attributed only to the accuracy of the spectrometers, and it is unclear what the exact of cause of this is. However, the errors found in both of these results raises the issue that there are errors inherent to this method and that normalising the data can magnify these significantly. As such, the accuracy of the chemical compositions has to be considered with caution – particularly as it is only possible to positively identify errors when they present as negative values.

Table 6-21 – Differences between actual and normalised composition of binders

	32b ACTUAL	32b NORMALISED	56b ACTUAL	56b NORMALISED
Al_2O_3	3.7	8.1	5.4	15.9
CaO	40.3	88.4	12.4	36.3
Cl	0.3	0.6	0.0	-0.1
Fe_2O_3	2.9	6.3	3.1	9.0
K_2O	0.4	0.9	0.7	2.0
MgO	0.9	1.9	-1.0	-3.1
MnO	0.1	0.1	0.0	-0.1
Na_2O	0.0	-0.1	0.7	2.2
P_2O5	0.2	0.5	0.2	0.7
SiO_2	-4.8	-10.4	12.1	35.4
SO_3	1.5	3.2	0.3	1.0
Sr	0.0	0.0	0.0	-0.1
TiO_2	0.2	0.4	0.3	0.8
Sum	*45.6*	*100.0*	*34.1*	*100.0*

Trends in Binder Results

The results of the chemical analyses are summarised in Table 6-22, and Figure 6-2 to Figure 6-7. However, it should be noted that these do not include the previously discussed erroneous data for samples 32b and 56b, or the chemical data of samples for which it was not possible to determine an age. In the case of samples where the age could only to be determined to be within a certain range, and not to an exact year, the average of this range was used to graph the data.

As was discussed throughout Chapter 2, the era from which these samples originate represents a period of experimentation, during which there was very little control over the cement manufacturing process, both in terms of the raw materials used and the manufacturing technology. However, the first Portland cement standard, introduced in 1904, contained specification for chemical composition which limited the insoluble residue, magnesia (MgO), and sulfuric anhydride (SO_3) contents to 1.5%, 3.0% and 2.5%, respectively. Furthermore, it limited the proportion of lime to silica and alumina, stating that it should not exceed the following limit (The Engineering Standards Committee, 1904):

$$\frac{CaO}{SiO_2 + Al_2O_3} = 2.75 \quad (48)$$

This limit was later revised with a modified equation in subsequent editions of the specification for Portland cement, as discussed in Chapter 2.2.4, to be within the range 2.0 to 3.0. As such, this presents one benchmark for comparison with the chemical analyses results of the samples in this study, as shown in Figure 6-8. Furthermore, the typical chemical composition of modern ordinary Portland cement (CEM I) is readily available, as discussed in Chapter 2.2.5, and this provides another benchmark for comparison – as shown in Figure 6-2 to Figure 6-7. However, as discussed in Chapter 2.2.2.1, the four historic cement works that were located in Scotland also produced blastfurnace slag cement. Therefore, it is possible that the chemical composition of some Scottish cements may be closer to that of modern CEM III.

In review of the chemical analyses, it is clear that, while results for MgO and SO_3 fall within levels which are comparable to modern Portland cements, Al_2O_3 and Fe_2O_3 are higher, and the levels of CaO and SiO_2 range significantly – with most falling well outside the typical range for modern cements. It is unclear if this range is due to the lack of control

of raw materials, varying methods of cement production, or errors in the chemical analysis of these samples. However, given that the ratio of CaO to SiO_2 and Al_2O_3 was controlled via equation (48) as early as 1904, and that most of the results obtained in this study fall outside the acceptable range imposed in the specification for Portland cement after 1915 (as shown in Figure 6-8), it seems likely that the determination of CaO and SiO_2 contents is flawed – most likely for the reasons that have already been discussed. As such, this further casts doubt on the available methods of determining the chemical composition of historic Portland cements through analysis of hardened concrete.

Table 6-22 – Summary of binder major oxide results

	CaO	**SiO_2**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**SO_3**
	%	***%***	***%***	***%***	***%***	***%***
Maximum	74.0	50.7	8.7	20.1	18.1	5.0
Minimum	16.1	4.3	1.2	4.2	2.3	0.3
Mean	39.9	32.3	3.4	11.7	7.5	1.7
Median	37.0	35.2	3.0	11.8	6.7	1.5
Standard Deviation	14.9	12.1	1.6	3.4	3.5	1.0
Mean Deviation	12.5	10.2	1.2	2.8	2.9	0.8

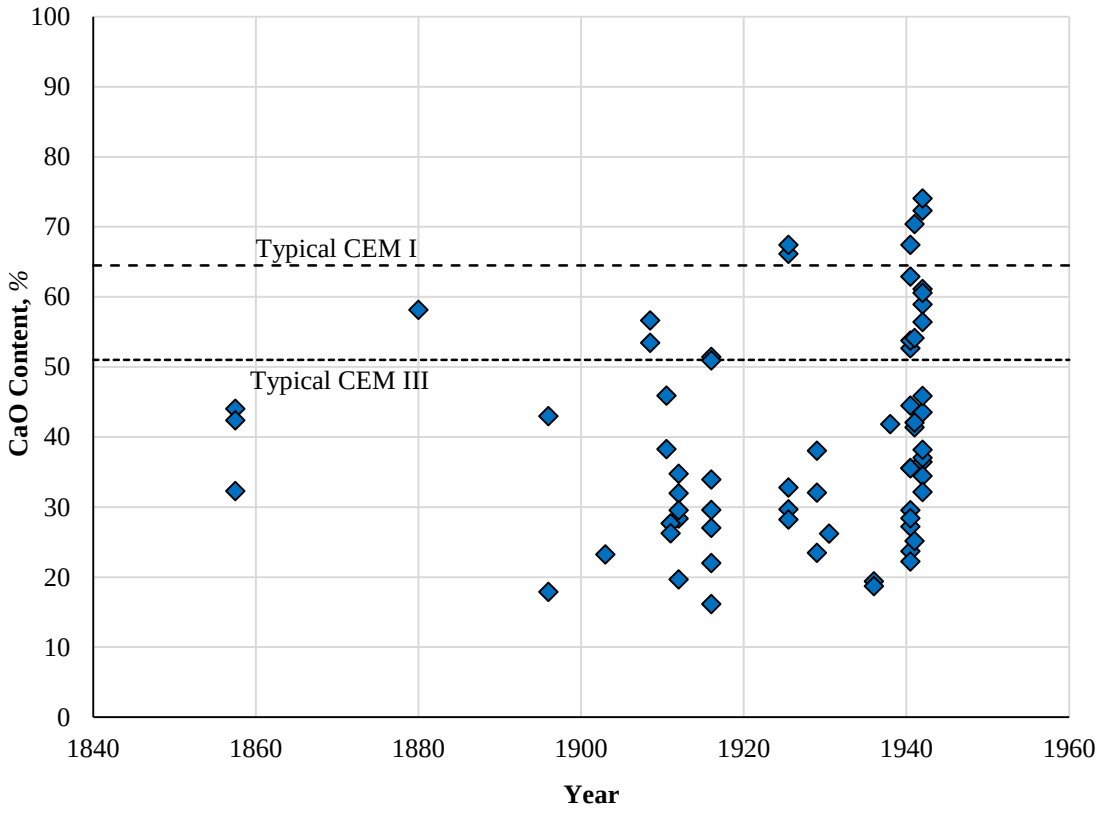

Figure 6-2 – CaO content of analysed samples and typical content of CEM I and CEM III

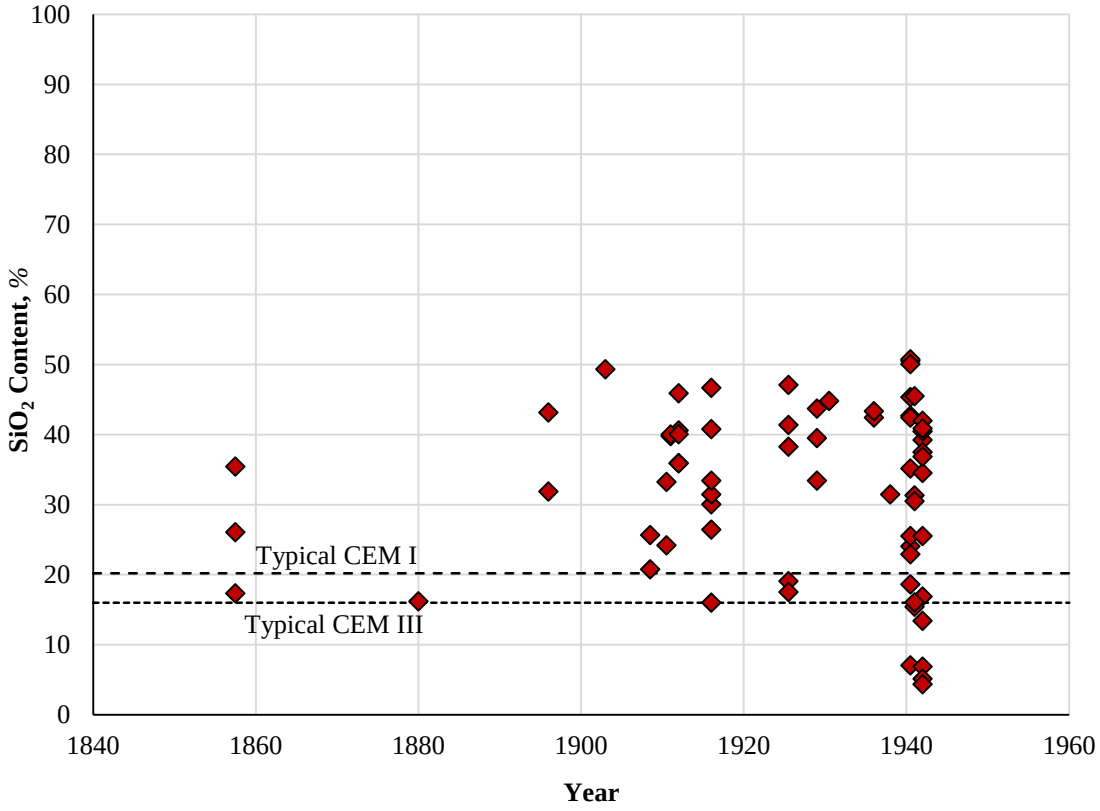

Figure 6-3 – SiO_2 content of analysed samples and typical content of CEM I and CEM III

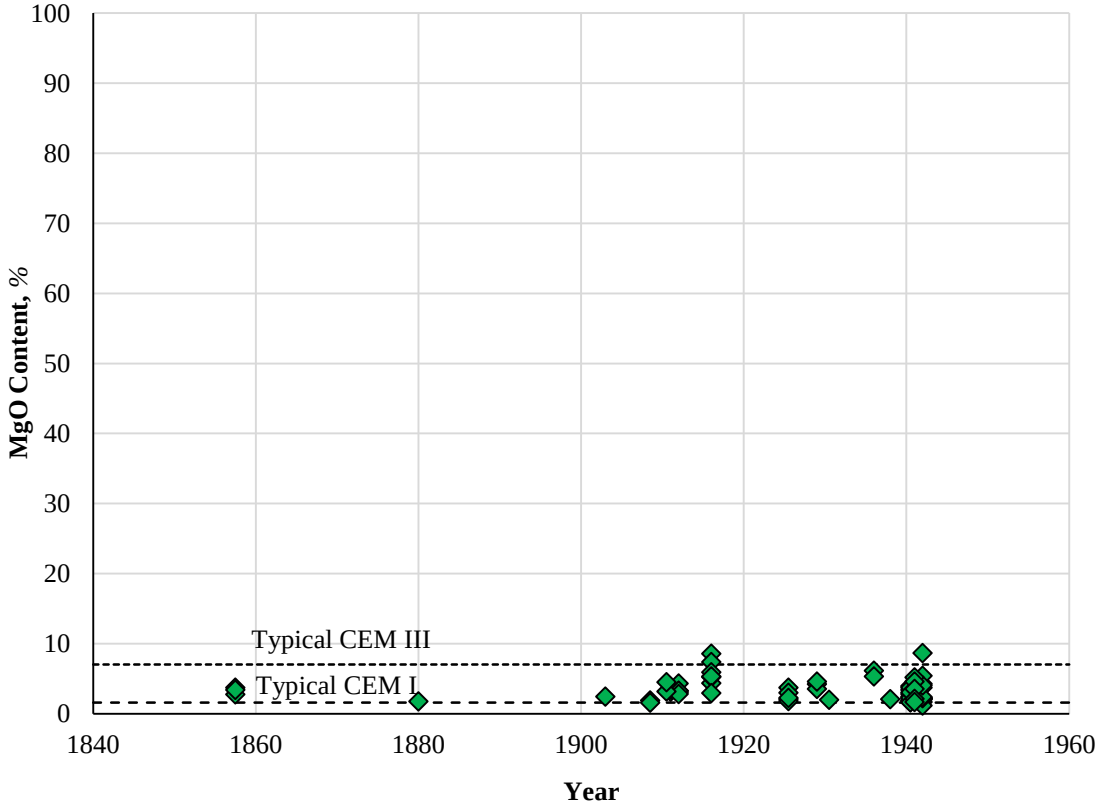

Figure 6-4 – MgO content of analysed samples and typical content of CEM I and CEM III

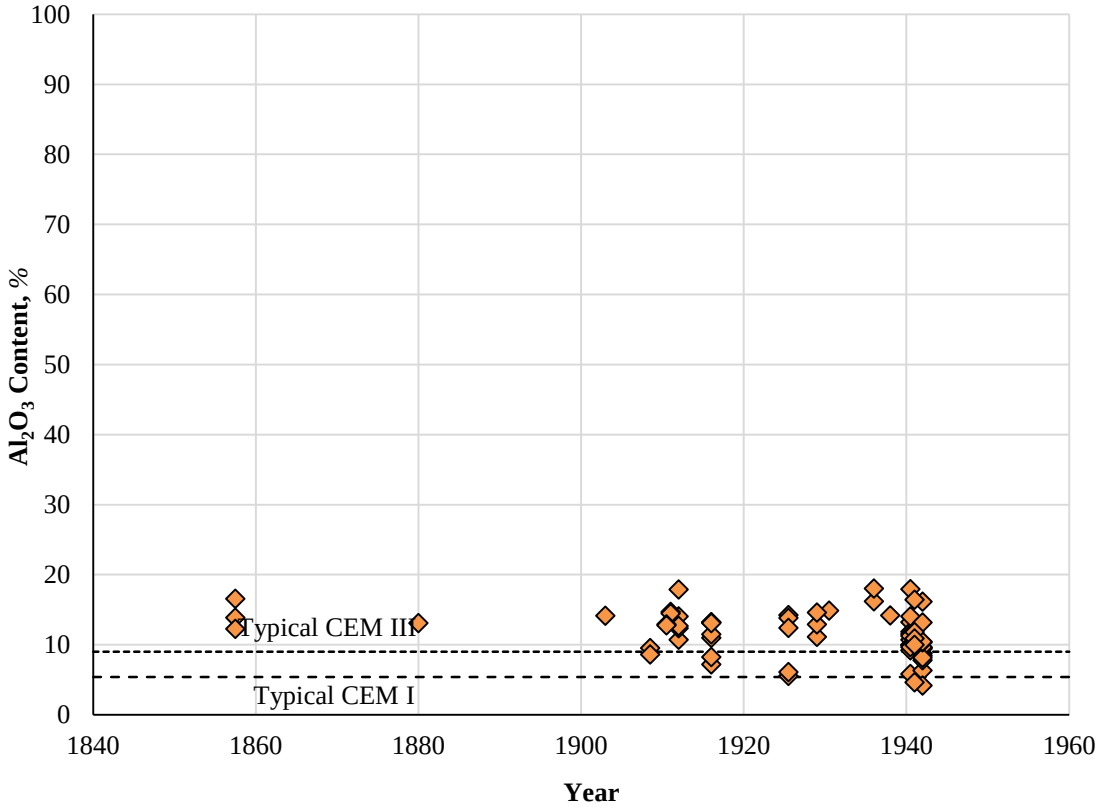

Figure 6-5 – Al_2O_3 content of analysed samples and typical content of CEM I and CEM III

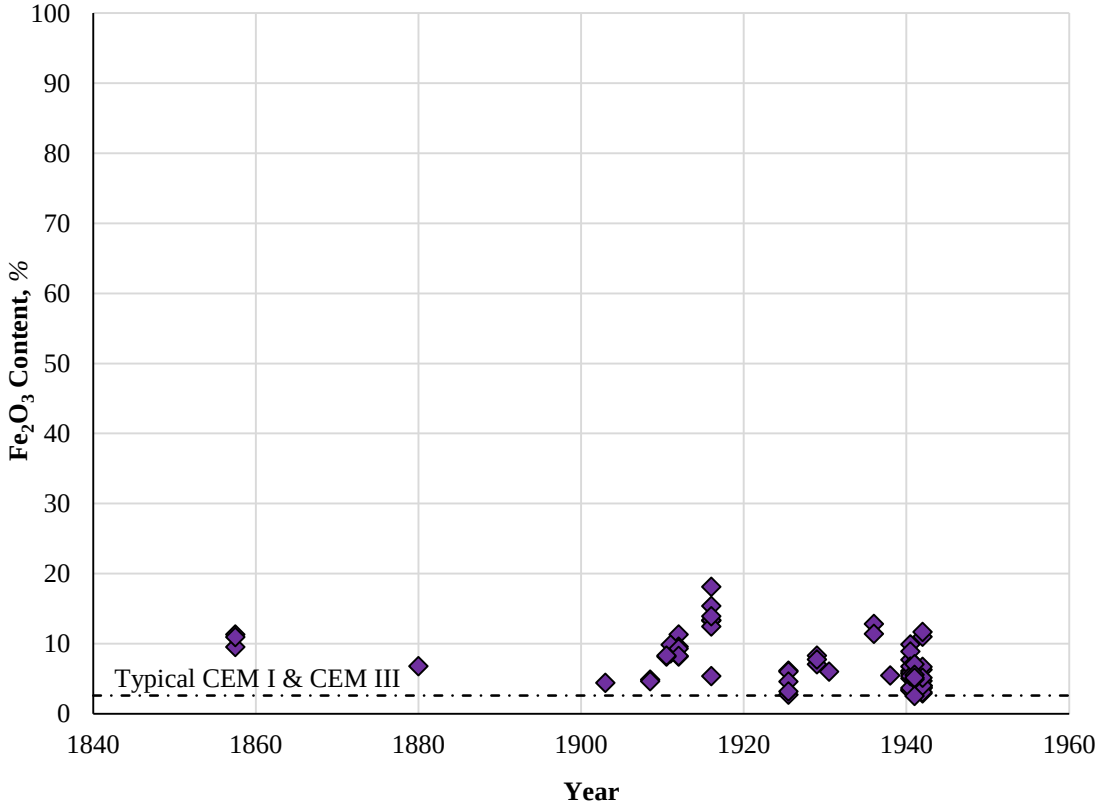

Figure 6-6 – Fe_2O_3 content of analysed samples and typical content of CEM I and CEM III

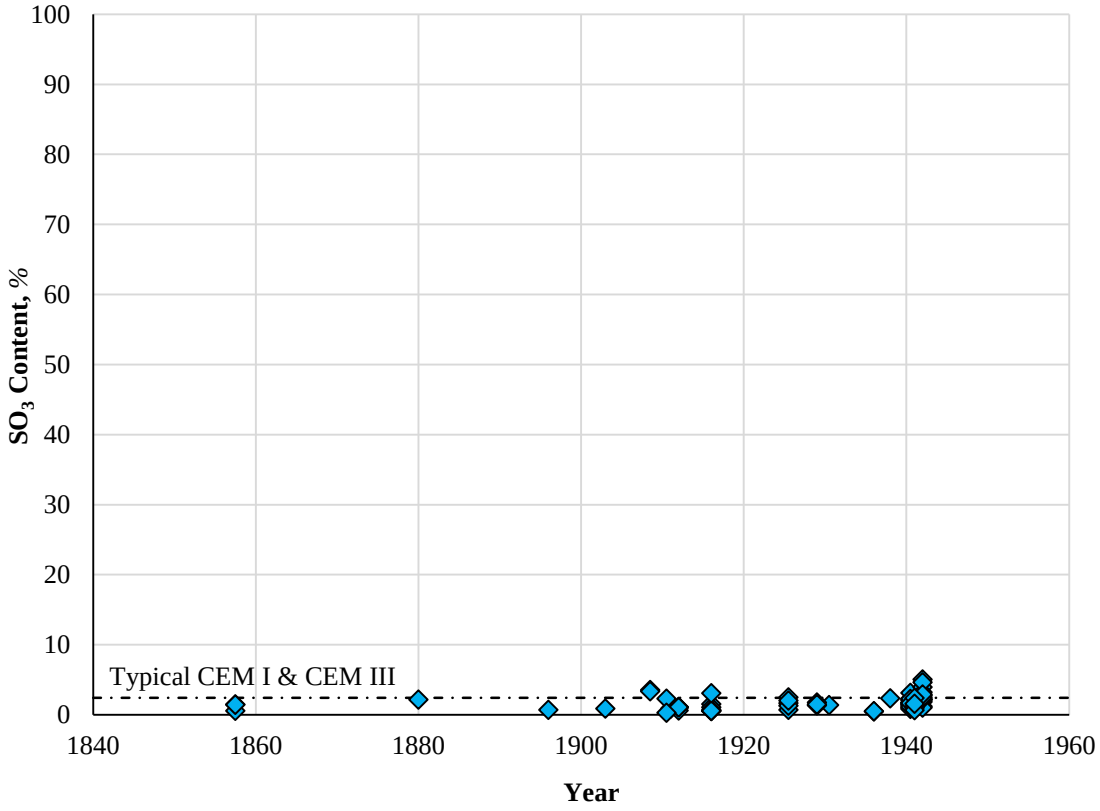

Figure 6-7– SO_3 content of analysed samples and typical content of CEM I and CEM III

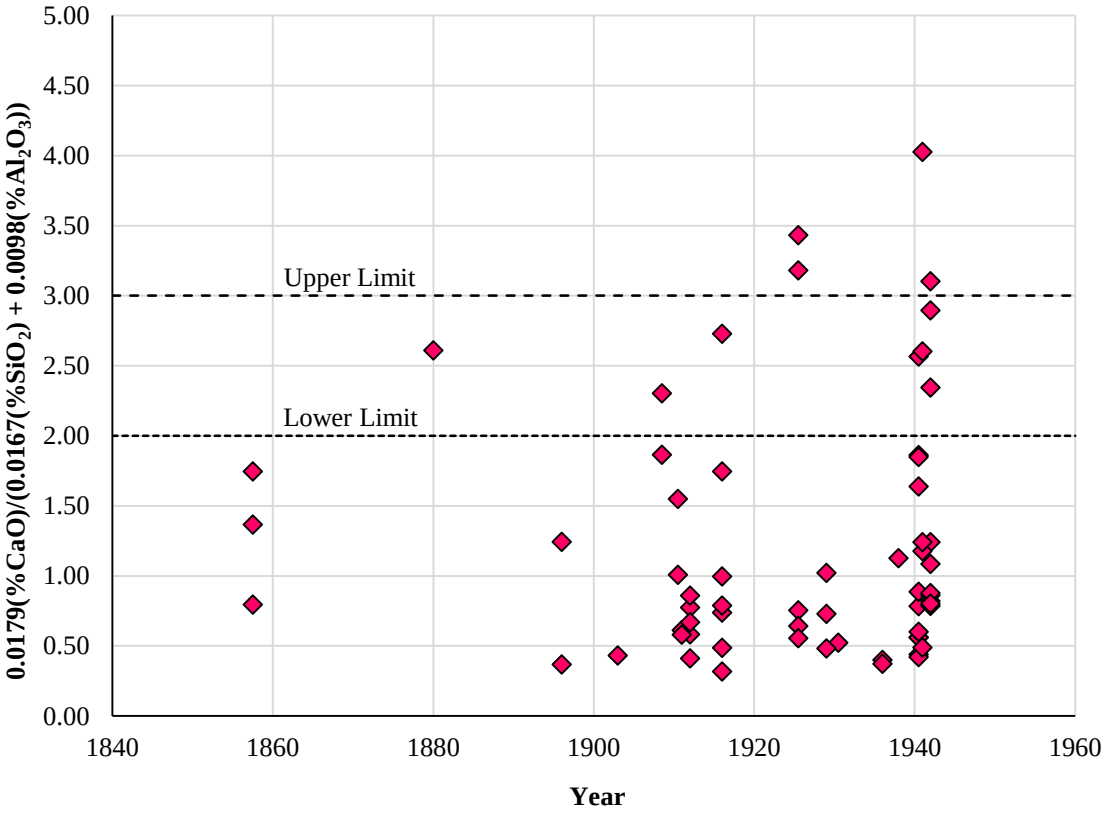

Figure 6-8 – Summary of CaO to SiO_2 and Al_2O_3 for analysed samples

6.3.3 Mineralogy

6.3.3.1 Concrete

Table 6-23 – Mineralogical composition of powdered concrete, part 1 of 5 (samples 01-17)

MINERAL	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17
Albite	-	-	4.3	1.2	1.4	3.9	14.3	8.7	14.3	17.6	8.6	15.1	24.2	11.3	13.8	33.2	16.8
Alite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.7	-
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Belite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Calcite	12.1	-	3.2	2.1	4.4	2.9	3.8	8.4	5.4	10.0	4.4	13.1	23.1	23.8	2.6	10.8	8.1
Chlorite	-	-	6.8	9.6	5.8	3.6	8.9	6.3	11.6	3.1	4.4	2.0	3.3	2.6	1.1	3.5	2.1
Cordierite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	5.5	1.8	-	-	-
Microcline	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Muscovite	-	-	29.5	32.2	26.4	26.5	50.3	46.3	43.6	33.0	51.0	49.0	0.7	0.8	0.9	1.7	4.2
Portlandite	0.3	-	0.9	0.4	0.5	0.6	0.9	0.6	3.4	-	-	0.8	-	-	-	-	-
Quartz	32.0	-	27.3	30.2	15.4	16.5	21.9	26.1	21.6	16.9	31.5	20.0	8.8	7.8	19.4	42.0	22.8
Sanidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.8	-
Crystalline Sum	*44.4*	-	*72.0*	*75.7*	*53.8*	*53.9*	*100.0*	*96.4*	*100.0*	*80.6*	*100.0*	*100.0*	*65.4*	*48.1*	*38.0*	*100.0*	*54.2*
Amorphous Sum	*55.6*	-	*28.0*	*24.3*	*46.2*	*46.1*	-	*3.6*	-	*19.4*	-	-	*34.6*	*51.9*	*62.0*	-	*45.8*

Table 6-24 – Mineralogical composition of powdered concrete, part 2 of 5 (samples 18-34)

MINERAL	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
Albite	5.4	3.5	8.2	2.4	5.2	6.2	1.2	-	17.2	-	-	6.9	7.3	2.5	3.6	3.5	7.9
Alite	-	0.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Belite	-	1.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	1.5	-	-	-	-	-
Calcite	4.7	10.4	0.5	1.1	16.7	28.9	13.2	13.6	17.2	-	-	4.3	16.6	9.0	20.3	13.1	8.0
Chlorite	1.2	1.2	0.3	0.8	4.3	3.1	1.0	-	4.1	-	-	-	-	-	-	-	0.5
Cordierite	-	-	-	2.0	-	-	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Microcline	-	-	-	2.6	-	6.1	0.9	-	-	-	-	-	-	1.8	-	2.2	7.8
Muscovite	0.4	2.4	-	3.7	10.2	9.5	-	-	2.3	-	-	-	-	-	-	-	1.3
Portlandite	0.4	2.0	-	-	2.7	-	-	0.3	-	-	-	3.0	0.7	-	-	-	-
Quartz	14.2	24.0	13.2	47.5	50.4	42.7	35.4	71.6	51.2	-	-	19.7	17.5	33.3	23.3	24.1	25.2
Sanidine	1.9	9.4	-	-	-	-	-	-	-	-	-	13.6	6.0	-	-	-	-
Crystalline Sum	*28.3*	*55.2*	*22.3*	*60.1*	*89.4*	*96.4*	*51.8*	*85.5*	*92.0*	-	-	*49.0*	*48.1*	*46.6*	*47.3*	*42.9*	*50.7*
Amorphous Sum	*71.7*	*44.8*	*77.7*	*39.9*	*10.6*	*3.6*	*48.2*	*14.5*	*8.0*	-	-	*51.0*	*51.9*	*53.4*	*52.7*	*57.1*	*49.3*

Table 6-25 – Mineralogical composition of powdered concrete, part 3 of 5 (samples 35-51)

MINERAL	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
Albite	8.4	-	26.4	16.5	2.6	4.5	10.2	-	0.3	14.5	22.5	12.9	1.8	18.0	1.5	3.2	1.5
Alite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.1
Anorthite	-	-	-	-	-	-	-	-	-	-	-	5.7	11.9	-	-	-	-
Belite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.9
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Calcite	10.9	41.0	7.7	6.0	2.2	14.5	9.8	-	1.4	1.6	1.6	6.6	4.6	0.7	2.2	13.7	15.1
Chlorite	0.6	-	-	1.8	-	1.0	1.0	-	-	4.4	2.9	0.4	0.6	0.9	0.8	1.6	0.8
Cordierite	-	-	-	-	-	-	-	-	-	5.4	2.3	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Microcline	2.1	-	5.8	-	2.9	9.4	4.0	-	-	-	-	-	-	-	-	3.8	1.4
Muscovite	0.8	-	-	4.2	-	3.2	2.1	-	-	-	-	3.5	3.7	3.0	-	3.6	2.0
Portlandite	-	-	0.9	-	4.5	-	-	-	-	0.4	-	0.7	1.0	0.3	3.8	-	-
Quartz	33.1	-	22.6	46.0	25.1	61.9	54.5	-	6.4	-	1.1	10.5	11.4	17.1	33.9	37.3	30.1
Sanidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Crystalline Sum	*56.0*	*41.3*	*63.5*	*74.6*	*37.4*	*94.4*	*81.7*	-	*8.1*	*26.4*	*30.4*	*40.2*	*35.0*	*40.0*	*42.2*	*63.5*	*54.0*
Amorphous Sum	*44.0*	*58.7*	*36.5*	*25.4*	*62.6*	*5.6*	*18.3*	-	*91.9*	*73.6*	*69.6*	*59.8*	*65.0*	*60.0*	*57.8*	*36.5*	*46.0*

Table 6-26 – Mineralogical composition of powdered concrete, part 4 of 5 (samples 51-68)

MINERAL	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68
Albite	7.4	-	-	-	17.9	43.6	20.9	21.0	0.9	17.4	4.6	-	0.7	9.3	2.9	1.9	5.6
Alite	1.5	-	-	-	-	-	-	-	0.5	0.9	-	-	-	-	3.2	0.3	0.9
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Belite	2.3	-	-	-	-	-	-	-	2.2	4.1	-	-	1.6	0.9	1.6	0.5	0.8
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Calcite	27.7	-	-	-	4.7	9.3	4.0	1.8	23.4	16.1	15.3	16.1	43.0	14.5	11.2	12.8	6.7
Chlorite	1.8	-	-	-	-	0.9	-	-	-	-	-	-	-	0.7	-	1.3	0.3
Cordierite	-	-	-	-	1.1	1.1	0.8	0.9	-	1.1	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Microcline	3.4	-	-	-	-	11.8	-	3.0	-	2.8	-	-	-	-	-	-	-
Muscovite	1.0	-	-	-	3.8	3.0	3.4	2.8	0.9	-	-	-	-	4.1	1.6	0.9	1.4
Portlandite	-	-	-	-	-	0.6	0.3	-	2.8	6.9	-	-	-	-	-	-	1.1
Quartz	36.1	-	-	-	13.1	29.7	15.8	12.6	3.5	7.5	50.9	45.8	31.3	28.1	28.4	7.4	36.8
Sanidine	-	-	-	-	-	-	-	-	0.3	-	3.3	1.4	-	6.5	3.6	6.1	1.3
Crystalline Sum	*81.3*	-	-	-	*40.6*	*100.0*	*45.1*	*42.2*	*34.5*	*56.9*	*74.3*	*63.3*	*76.8*	*64.2*	*53.1*	*31.1*	*54.9*
Amorphous Sum	*18.7*	-	-	-	*59.4*	-	*54.9*	*57.8*	*65.5*	*43.1*	*25.7*	*36.7*	*23.2*	*35.8*	*46.9*	*68.9*	*45.1*

Table 6-27 – Mineralogical composition of powdered concrete, part 5 of 5 (samples 69-85)

MINERAL	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85
Albite	16.5	4.8	6.6	0.5	6.7	9.0	-	6.0	9.7	2.0	6.7	1.0	-	-	-	9.3	10.7
Alite	-	4.1	-	0.7	-	-	-	-	-	-	-	-	-	-	-	-	1.1
Anorthite	-	-	-	-	-	-	-	-	-	-	-	2.2	-	-	-	-	-
Belite	-	8.5	1.9	1.3	-	-	-	-	-	-	-	-	-	-	-	-	0.9
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.5
Calcite	15.0	18.6	19.2	13.2	13.8	2.0	-	13.9	15.4	7.7	13.2	19.2	-	-	-	3.2	7.0
Chlorite	1.8	0.8	0.5	-	-	1.8	0.6	0.7	0.8	1.3	-	-	-	-	-	1.2	0.4
Cordierite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	1.2	-	-	-	-	-	-	-	-	-	-	4.7	-
Microcline	-	6.2	11.1	0.6	-	0.9	-	-	5.6	1.8	-	0.9	-	-	-	-	3.1
Muscovite	1.0	1.4	1.1	-	0.7	3.0	-	3.7	3.9	6.1	6.8	0.5	-	-	-	0.4	-
Portlandite	-	9.5	1.1	0.5	-	2.5	-	-	-	-	-	1.5	-	-	-	-	-
Quartz	22.7	38.8	39.1	37.9	5.4	20.8	43.3	31.8	35.9	25.9	61.9	5.8	-	-	-	3.5	8.9
Sanidine	8.5	-	-	-	9.8	-	-	12.8	-	-	5.4	-	-	-	-	4.0	-
Crystalline Sum	*65.7*	*92.6*	*80.7*	*54.6*	*37.6*	*40.0*	*43.9*	*68.8*	*71.4*	*44.8*	*94.0*	*31.1*	-	-	-	*26.2*	*34.8*
Amorphous Sum	*34.3*	*7.4*	*19.3*	*45.4*	*62.4*	*60.0*	*56.1*	*31.2*	*28.6*	*55.2*	*6.0*	*68.9*	-	-	-	*73.8*	*65.2*

6.3.3.2 Aggregate

Table 6-28 – Mineralogical composition of insoluble residue, part 1 of 5 (samples 01a-17a)

MINERAL	01a	02a	03a	04a	05a	06a	07a	08a	09a	10a	11a	12a	13a	14a	15a	16a	17a
Albite	-	-	10.7	9.4	7.3	14.5	7.0	11.1	4.2	15.8	8.8	14.4	3.9	43.3	29.6	20.4	26.7
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	8.6	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorite	-	-	2.7	4.4	1.1	2.6	1.2	3.6	3.9	1.8	1.7	1.5	-	2.1	-	0.3	0.7
Cordierite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	6.4	-	-	-
Microcline	0.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Muscovite	-	-	24.7	17.0	19.1	18.9	26.5	23.2	18.2	16.5	24.0	32.6	0.7	2.8	0.6	2.2	6.8
Quartz	74.7	-	8.0	26.3	23.4	16.2	23.3	25.3	22.3	18.9	52.3	25.6	20.1	36.0	33.4	39.9	38.3
Sanidine	-	-	-	-	-	-	-	-	-	-	-	-	5.3	-	-	11.4	-
Crystalline Sum	*75.5*	-	*46.1*	*57.1*	*50.9*	*52.2*	*58.0*	*63.2*	*48.6*	*53.0*	*86.8*	*74.0*	*38.8*	*90.6*	*63.7*	*74.2*	*72.6*
Amorphous Sum	*24.5*	-	*53.9*	*42.9*	*49.1*	*47.8*	*42.0*	*36.8*	*51.4*	*47.0*	*13.2*	*26.0*	*61.2*	*9.4*	*36.3*	*25.8*	*27.4*

Table 6-29 – Mineralogical composition of insoluble residue, part 2 of 5 (samples 18a-34a)

MINERAL	18a	19a	20a	21a	22a	23a	24a	25a	26a	27a	28a	29a	30a	31a	32a	33a	34a
Albite	11.4	2.9	23.0	1.6	5.4	3.1	4.0	-	18.9	-	-	2.1	6.9	2.0	31.7	31.7	3.9
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	1.9	-	-	-	-	-
Chlorite	0.5	0.5	0.5	0.5	1.1	0.7	1.0	-	4.0	-	-	-	-	-	-	-	0.3
Cordierite	-	-	-	1.1	-	-	-	-	-	-	-	-	-	-	0.6	0.6	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	2.1	-	-	-	-	-	-	-	-
Microcline	-	-	-	0.3	1.8	6.2	2.1	-	-	-	-	-	-	1.5	-	-	3.1
Muscovite	1.1	0.8	1.2	5.3	5.2	4.5	0.9	-	4.2	-	-	-	-	-	-	-	0.8
Quartz	28.0	45.1	21.5	58.2	49.9	47.4	68.8	47.4	41.3	-	-	10.6	47.9	40.4	62.2	62.2	43.4
Sanidine	2.7	1.9	-	-	-	-	-	-	-	-	-	12.6	1.3	-	-	-	-
Crystalline Sum	*43.7*	*51.2*	*46.3*	*66.9*	*63.3*	*61.9*	*76.7*	*47.4*	*70.4*	-	-	*27.2*	*56.1*	*43.9*	*94.5*	*94.5*	*51.6*
Amorphous Sum	*56.3*	*48.8*	*53.7*	*33.1*	*36.7*	*38.1*	*23.3*	*52.6*	*29.6*	-	-	*72.8*	*43.9*	*56.1*	*5.5*	*5.5*	*48.4*

Table 6-30 – Mineralogical composition of insoluble residue, part 3 of 5 (samples 35a-51a)

MINERAL	35a	36a	37a	38a	39a	40a	41a	42a	43a	44a	45a	46a	47a	48a	49a	50a	51a
Albite	9.7	-	19.3	5.1	3.4	2.9	4.4	-	0.3	21.5	24.0	19.6	3.8	12.8	1.5	2.8	7.5
Anorthite	-	-	-	-	-	-	-	-	-	-	-	8.5	11.9	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorite	-	-	-	0.4	-	-	0.3	-	-	4.7	2.1	0.4	-	0.4	-	0.6	1.1
Cordierite	-	-	0.7	-	-	-	-	-	-	5.9	2.5	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Microcline	4.1	-	10.0	-	7.5	1.6	1.2	-	-	-	-	-	-	-	-	1.8	3.0
Muscovite	1.2	-	-	3.4	0.5	-	0.7	-	-	-	-	3.9	0.8	0.7	-	1.9	3.4
Quartz	36.8	0.7	14.0	33.1	43.5	67.9	50.4	-	6.9	0.6	1.1	16.7	18.1	24.0	49.5	54.3	65.2
Sanidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Crystalline Sum	*52.0*	*0.7*	*44.0*	*42.0*	*54.9*	*72.5*	*56.9*	-	*7.2*	*32.7*	*29.6*	*49.1*	*34.8*	*37.9*	*51.1*	*61.4*	*80.0*
Amorphous Sum	*48.0*	*99.3*	*56.0*	*58.0*	*45.1*	*27.5*	*43.1*	-	*92.8*	*67.3*	*70.4*	*50.9*	*65.2*	*62.1*	*48.9*	*38.6*	*20.0*

Table 6-31 – Mineralogical composition of insoluble residue, part 4 of 5 (samples 52a-68a)

MINERAL	52a	53a	54a	55a	56a	57a	58a	59a	60a	61a	62a	63a	64a	65a	66a	67a	68a
Albite	5.7	-	-	-	41.9	34.8	31.3	18.6	14.6	14.4	2.4	0.5	2.4	13.1	5.2	11.6	4.0
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlorite	0.6	-	-	-	-	0.3	-	-	-	-	-	-	-	1.3	-	1.2	-
Cordierite	-	-	-	-	1.7	0.9	0.8	0.4	0.6	1.2	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Microcline	1.8	-	-	-	-	10.4	-	1.8	-	13.0	-	-	-	-	-	-	-
Muscovite	1.2	-	-	-	5.1	1.4	4.2	0.6	-	-	-	-	-	2.1	2.4	0.9	-
Quartz	52.1	-	-	-	37.3	22.5	25.1	14.7	18.9	30.0	53.0	59.3	48.9	30.7	51.1	57.8	41.1
Sanidine	-	-	-	-	-	-	-	-	2.7	-	2.7	0.8	-	0.9	3.1	21.0	2.1
Crystalline Sum	*61.5*	-	-	-	*86.0*	*70.3*	*61.5*	*36.2*	*36.8*	*58.7*	*58.1*	*60.6*	*51.3*	*48.1*	*62.0*	*92.6*	*47.1*
Amorphous Sum	*38.5*	-	-	-	*14.0*	*29.7*	*38.5*	*63.8*	*63.2*	*41.3*	*41.9*	*39.4*	*48.7*	*51.9*	*38.0*	*7.4*	*52.9*

Table 6-32 – Mineralogical composition of insoluble residue, part 5 of 5 (samples 69a-85a)

MINERAL	69a	70a	71a	72a	73a	74a	75a	76a	77a	78a	79a	80a	81a	82a	83a	84a	85a
Albite	19.7	10.0	0.9	1.0	12.7	17.5	32.9	8.4	8.7	5.3	2.4	7.6	-	-	-	11.4	18.2
Anorthite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Biotite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.7
Chlorite	2.1	-	-	-	-	1.4	0.4	0.4	-	-	-	-	-	-	-	0.5	0.5
Cordierite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.1	-
Microcline	-	6.0	5.1	6.3	2.4	11.7	-	-	1.6	3.5	-	2.7	-	-	-	-	-
Muscovite	1.3	2.3	-	-	2.4	1.7	-	4.6	2.9	2.9	1.0	1.9	-	-	-	0.9	11.0
Quartz	38.6	78.1	89.9	89.4	9.6	61.2	-	66.6	47.5	39.5	45.1	41.1	-	-	-	6.2	16.7
Sanidine	11.0	-	-	-	18.6	-	-	10.4	-	-	2.3	-	-	-	-	4.4	-
Crystalline Sum	*72.8*	*96.4*	*95.8*	*96.7*	*45.8*	*93.6*	*33.3*	*90.5*	*60.8*	*51.4*	*50.8*	*53.3*	-	-	-	*28.3*	*50.1*
Amorphous Sum	*27.2*	*3.6*	*4.2*	*3.3*	*54.2*	*6.4*	*66.7*	*9.5*	*39.2*	*48.6*	*49.2*	*46.7*	-	-	-	*71.7*	*49.9*

Table 6-33 – Chemical composition of minerals in XRD analyses

MINERAL	COMPOSITION
Albite	$NaAlSi_3O_8$
Alite	Ca_3SiO_5
Anorthite	$CaAl_2Si_2O_8$
Belite	Ca_2SiO_4
Biotite	$KMg_{2.5}Fe^{2+}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$
Calcite	$CaCO_3$
Chlorite	$Mg_{3.75}Fe^{2+}_{1.25}Si_3Al_2O_{10}(OH)_8$
Cordierite	$Mg_2Al_4Si_5O_{18}$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Magnetite	$Fe^{3+}_2Fe^{2+}O_4$
Microcline	$KAlSi_3O_8$
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$
Portlandite	$Ca(OH)_2$
Quartz	SiO_2
Sanidine	$KAlSi_3O_8$

6.3.3.3 Discussion

It can be concluded from the XRD analyses of the insoluble residue that the aggregates found in these samples were predominantly quartz, feldspar (albite, anorthite, sanidine and microcline) and mica (chlorite, muscovite and some biotite). Variations in the aggregate mineralogy appear to vary with geographic location, suggesting the use of locally available aggregate.

This hypothesis is supported by the fact that many of the samples were from structures that were fairly remote and built at a time when Scotland's infrastructure was far less developed than it is today – making the transportation of large quantities of aggregate both time consuming and expensive. However, many of the sample locations that were in close geographical proximity to each other were so because they formed parts of the same structure or overall project, and so may not have been sourced locally but, instead, may have come from the same external quarry.

The link between aggregate compositions and geographical location can be examined further in two ways: Firstly, by comparing the XRD data for the insoluble residue – shown in Table 6-28 to Table 6-32 – to the inventory of historic specimens shown in

Table 3-1 to Table 3-4, it can be seen that samples from the same locations generally had similar aggregates. For example, samples 03-09 from Arklet Dam (1911-1912) and samples 10-12 from the nearby Loch Katrine (1856-1859) contained aggregates with similar mineralogical compositions. Secondly, this data can be examined in a broader, national context, such as in Figure 6-9 to Figure 6-15, which show the differences in concentration of particular aggregate minerals across Scotland. While the limited number of sample locations makes it difficult to determine any definite trends, this initial data suggests a link which could warrant further investigation as more data regarding the mineralogical composition of historic aggregates becomes available.

Analysis of the powdered concrete samples revealed they contained very little of the hydration product portlandite (calcium hydroxide) or the clinker components alite and belite – with the majority of the binder being calcite (calcium carbonate). The lack of clinker components suggests that the majority of the Portland cement in the concrete samples had fully hydrated and, as the binders were predominantly calcite, this indicates that the hydration products have subsequently reacted with atmospheric carbon dioxide. However, full hydration of the cement paste and significant carbonation are to be expected given the age of these samples.

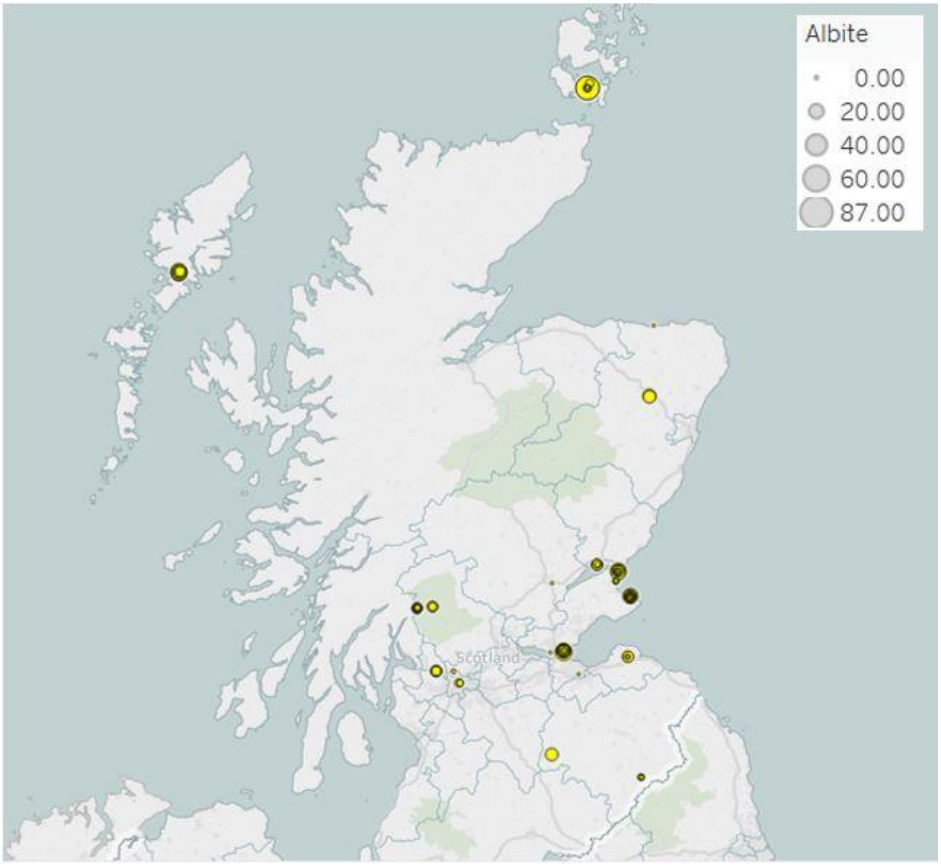

Figure 6-9 – Albite concentrations as a percentage of aggregate, mapped by site location

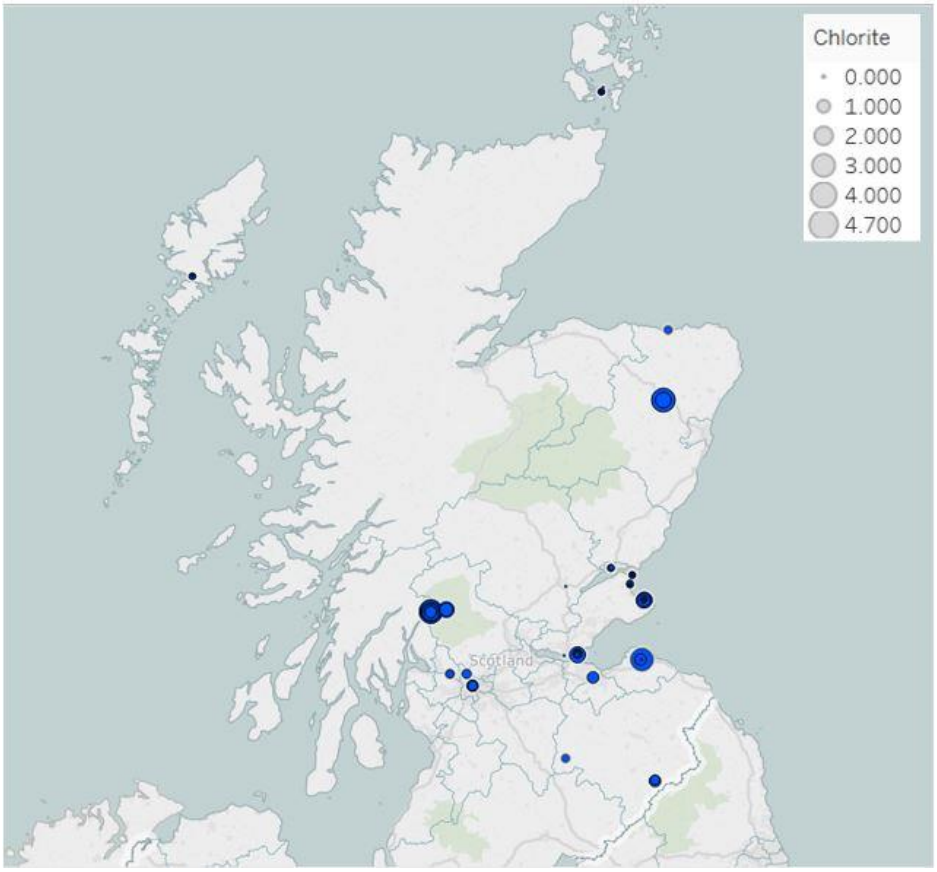

Figure 6-10 – Chlorite concentrations as a percentage of aggregate, mapped by site location

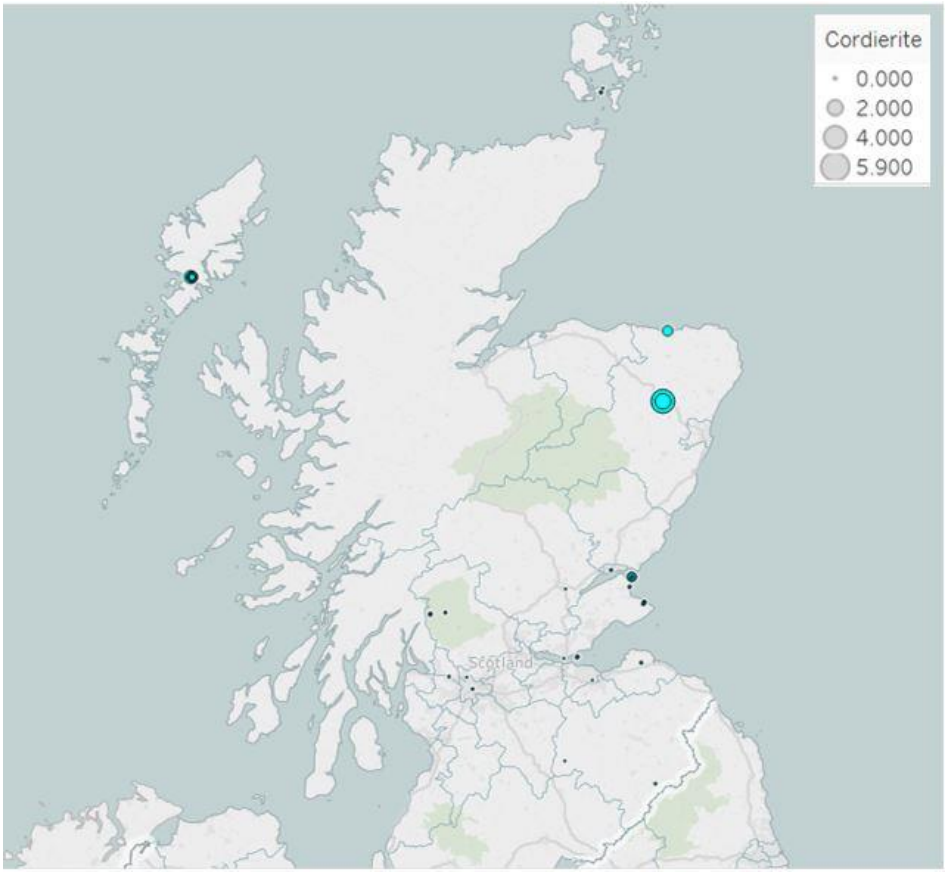

Figure 6-11 – Cordierite concentrations as a percentage of aggregate, mapped by site location

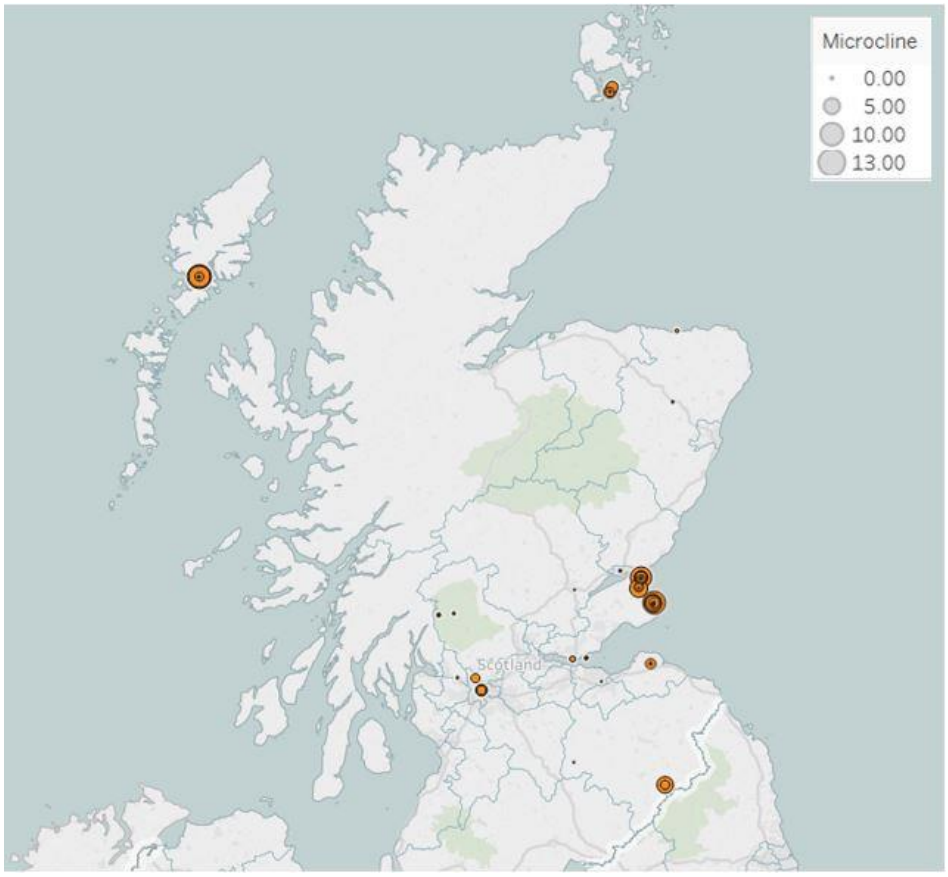

Figure 6-12 – Micrcline concentrations as a percentage of aggregate, mapped by site location

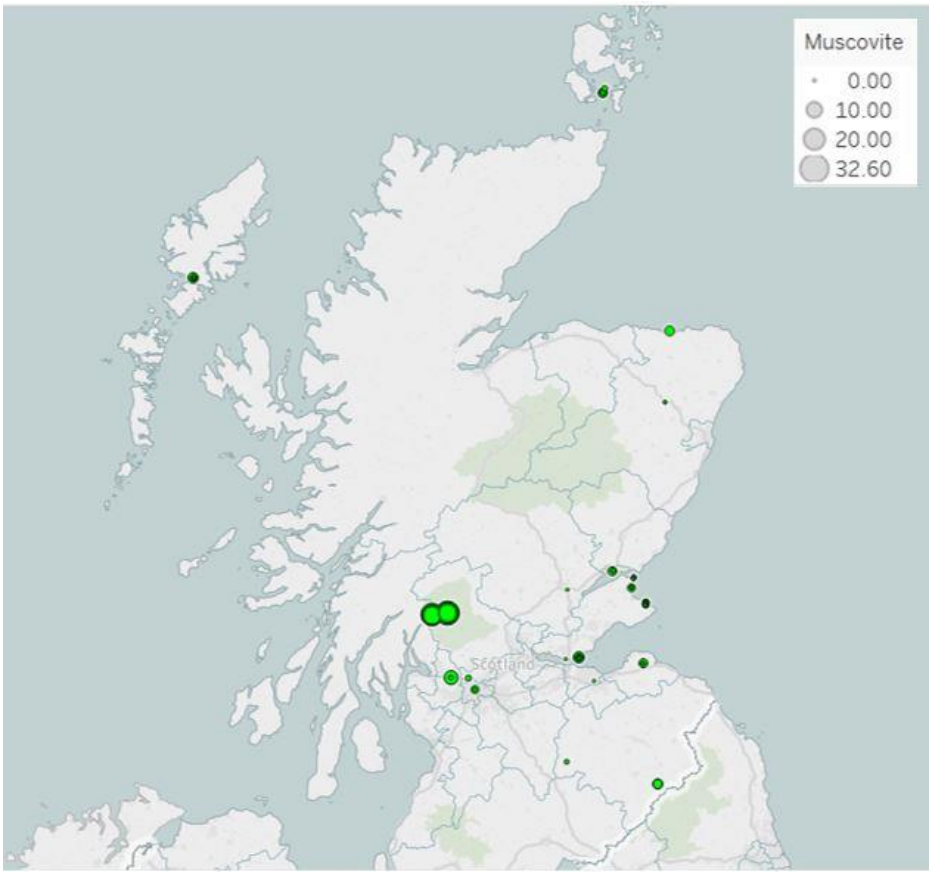

Figure 6-13 – Muscovite concentrations as a percentage of aggregate, mapped by site location

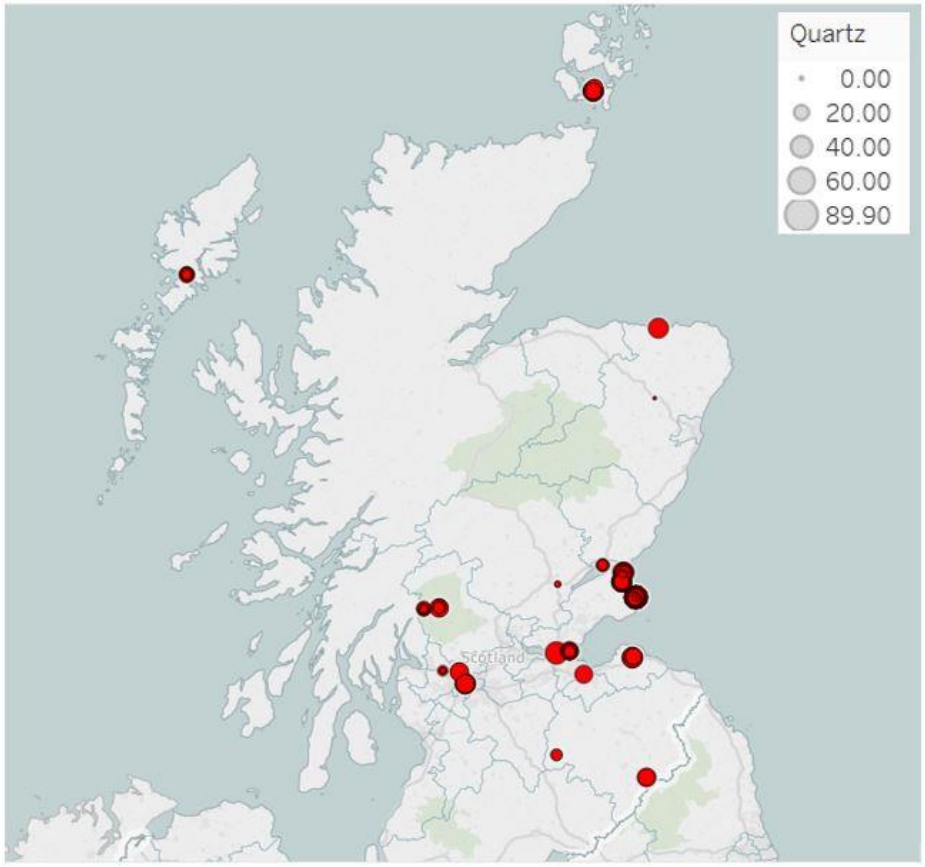

Figure 6-14 – Quartz concentrations as a percentage of aggregate, mapped by site location

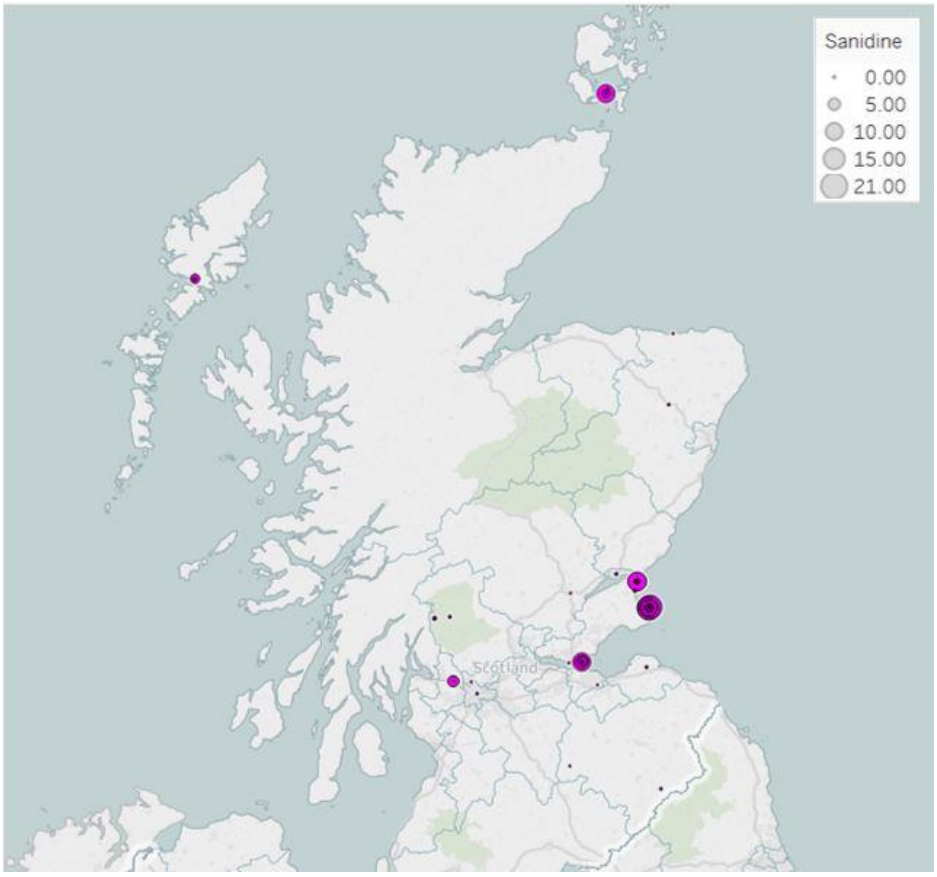

Figure 6-15 – Sanidine concentrations as a percentage of aggregate, mapped by site location

Issues associated with XRD

There are some issues inherent to quantitative XRD that need to be taken into consideration as they present sources of possible error. As well as the need for an internal standard to act as a reference for intensity (discussed in Chapter 3.3.5), the accurate quantification is complicated by factors such as particle size and orientation, the chemical and structural variations of certain minerals (Brindley, 1980), and the wide, overlapping peaks of different clay minerals, which result in poor peak separation (Lanson, 1997)

For example, the determination of intensity is dependent on the orientation of the mineral particles, and while the theoretical assumption is that particle orientation is random, the platy characteristics of clay minerals results in a preferred orientation of their particles – consequently influencing the recorded intensities of certain minerals (Brindley, 1980).

While action was taken during sample preparation to minimise the risk of preferred orientation, it is not possible to fully eliminate its influence. Furthermore, as many clay minerals display chemical and structural variations, this makes the choice of reference materials challenging, and this can lead to the selection of incorrect structural data (Brindley, 1980).

Therefore, even when every effort is taken to minimise these sources of error, it is likely that analyses of geological samples that include clay minerals can, at best, only be considered accurate to within ± 3% at the 95% confidence level (Hillier, 2000).

Alternatives to XRD

As quantitative microscopical analysis is regularly carried out on historic lime mortars, it can be argued that this technique should be applied in the forensic analyses of historic concrete in order to determine the overall aggregate content and to quantity the different aggregate minerals present. However, as discussed in Chapter 4, the heterogeneity of concrete is such that impractically large samples are required for accurate determinations. This is because the standards used in quantitative analyses require minimum sample sizes based on the maximum size of aggregate, which is significantly larger for concrete samples than it is for mortar.

As there are, at present, no British Standards for the quantitative microscopical analysis of hardened concrete, the American Standards, ASTM C 457 and ASTM C 856, are often used in the United Kingdom instead. The approximate sample sizes required to undertake

the quantitative point counting method described in ASTM C 457 (ASTM International, 1998) can be found in Table 6-34.

It is clear from Table 6-34 that, based on the minimum sample size that is required, the application of microscopical techniques for the quantitative analyses of historic concrete is completely impractical – especially given the observed maximum aggregate sizes discussed in Chapter 5.3 and the issues associated with obtaining samples discussed in Chapter 4.2. Therefore, while the analysis of thin sections can be useful in the identification of the various mineral phases in concrete, there is currently no adequate alternative to the use XRD for quantitatively determining the mineralogical composition.

Table 6-34 – Minimum area of finished surface for microscopical measurement

NOMINAL OR OBSERVED MAXIMUM SIZE OF AGGREGATE IN THE CONCRETE	TOTAL AREA TO BE TRAVERSED FOR MEASUREMENT	APPROXIMATE SAMPLE SIZE
mm	***cm^2***	***cm***
150	1613	40×40
75	419	21×21
37.5	155	13×13
25	77	9×9
19	71	9×9
12.5	65	8×8
9.5	58	8×8
4.75	45	7×7
3	36	6×6
1	12	4×4
0.5	6	3×3
0.25	3	2×2

Source: Goins (2004) adapted from ASTM 457 (1998)

6.3.4 Aggregate Particle Size Distribution

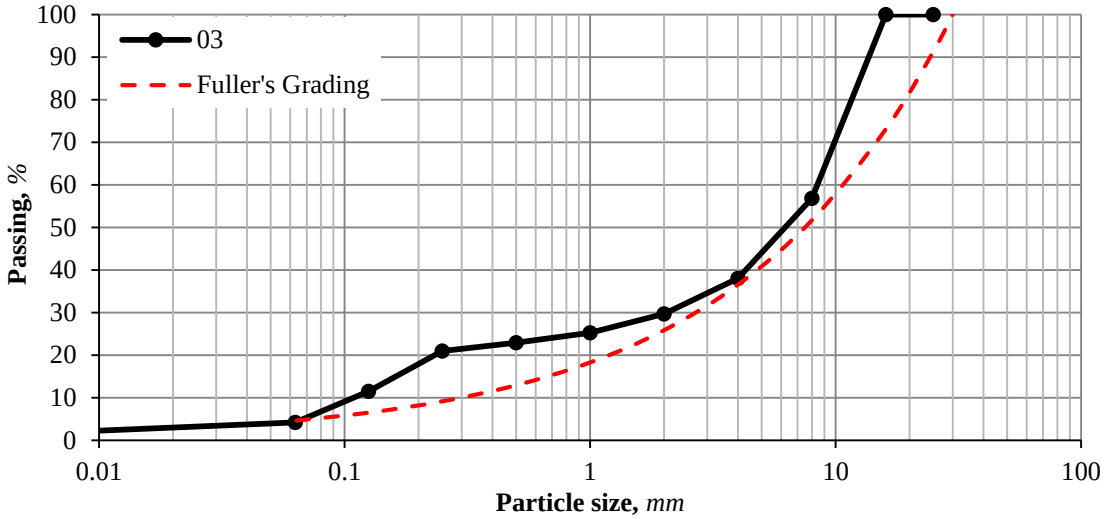

Figure 6-16 – Aggregate grading curve of sample 03

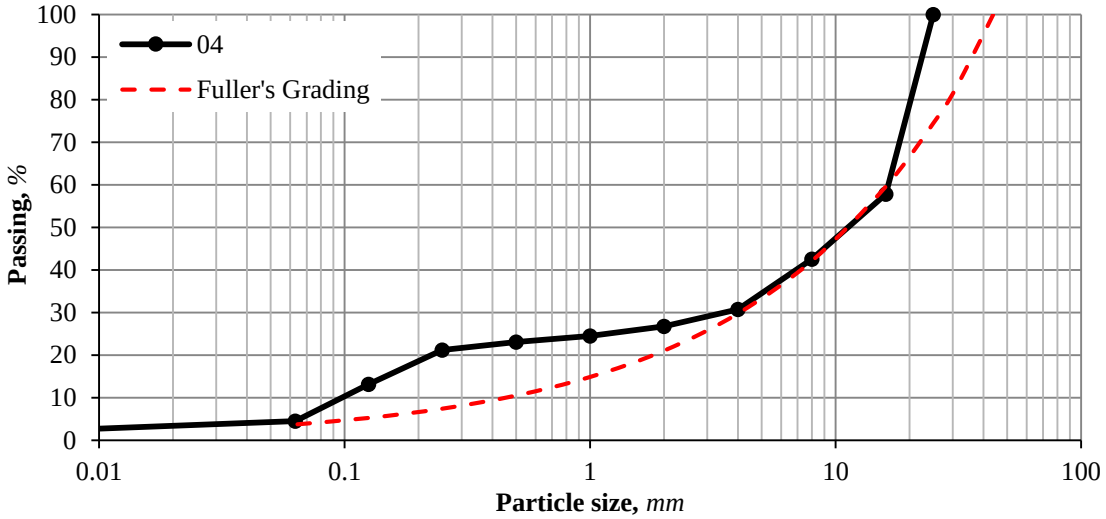

Figure 6-17 – Aggregate grading curve of sample 04

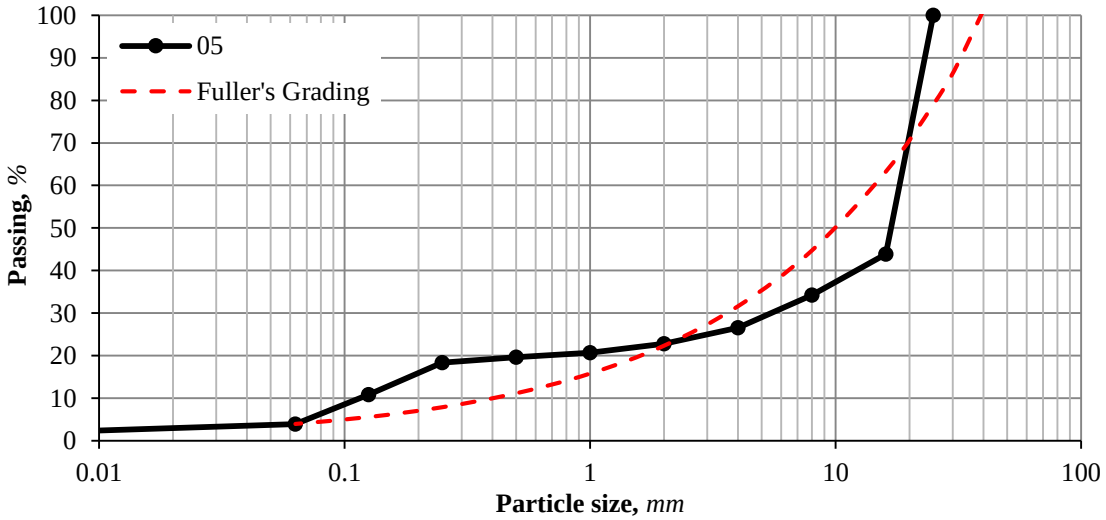

Figure 6-18 – Aggregate grading curve of sample 05

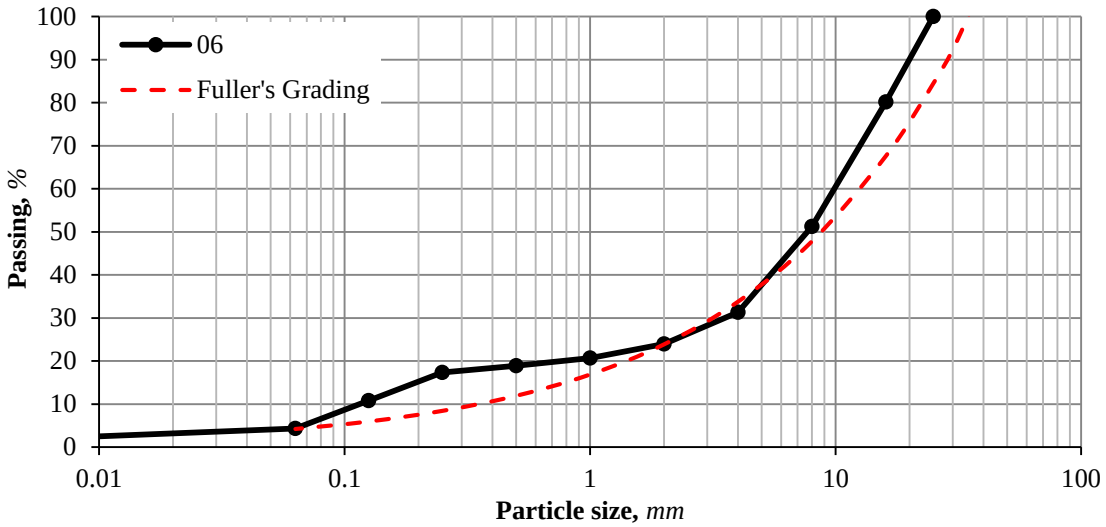

Figure 6-19 – Aggregate grading curve of sample 06

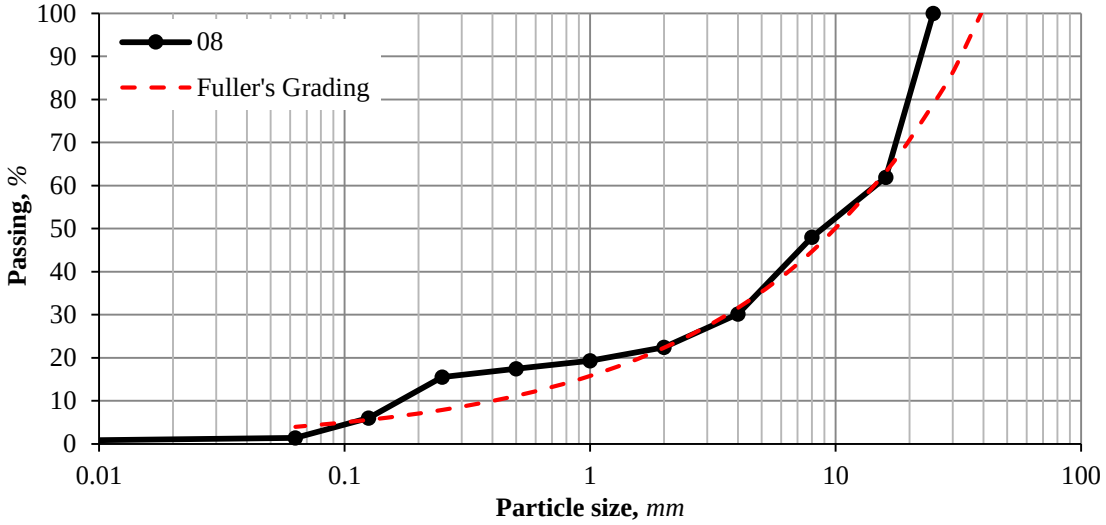

Figure 6-20 – Aggregate grading curve of sample 08

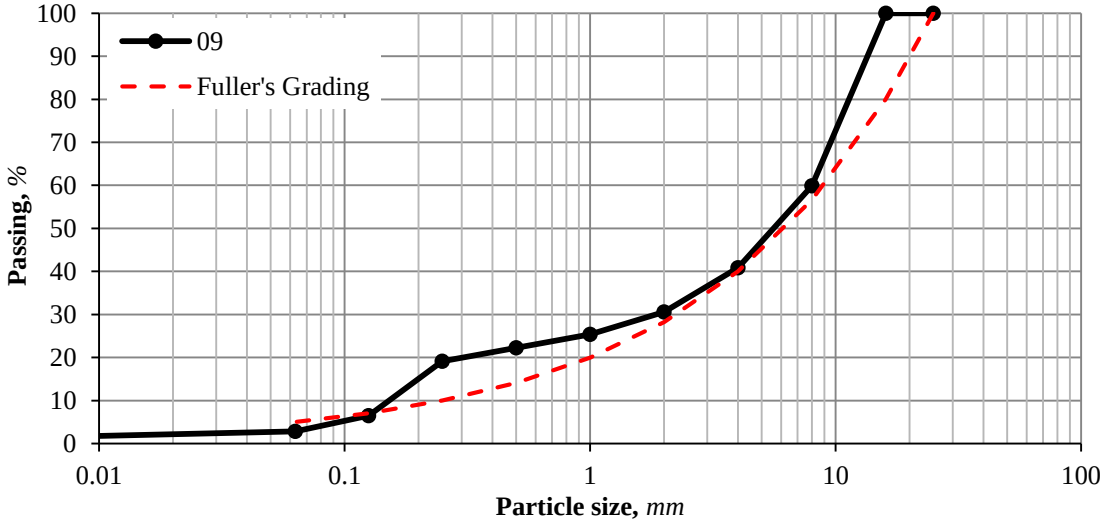

Figure 6-21 – Aggregate grading curve of sample 09

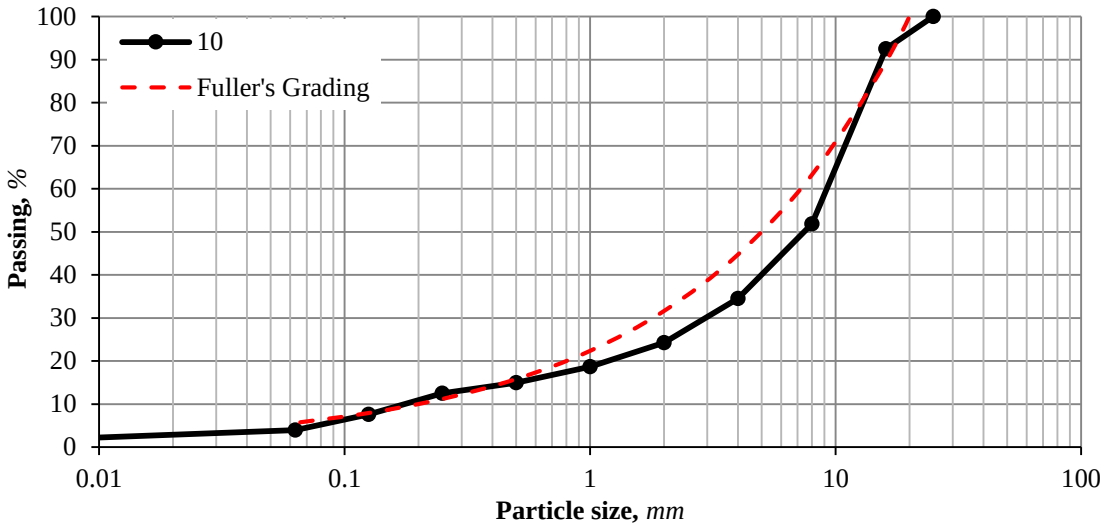

Figure 6-22 – Aggregate grading curve of sample 10

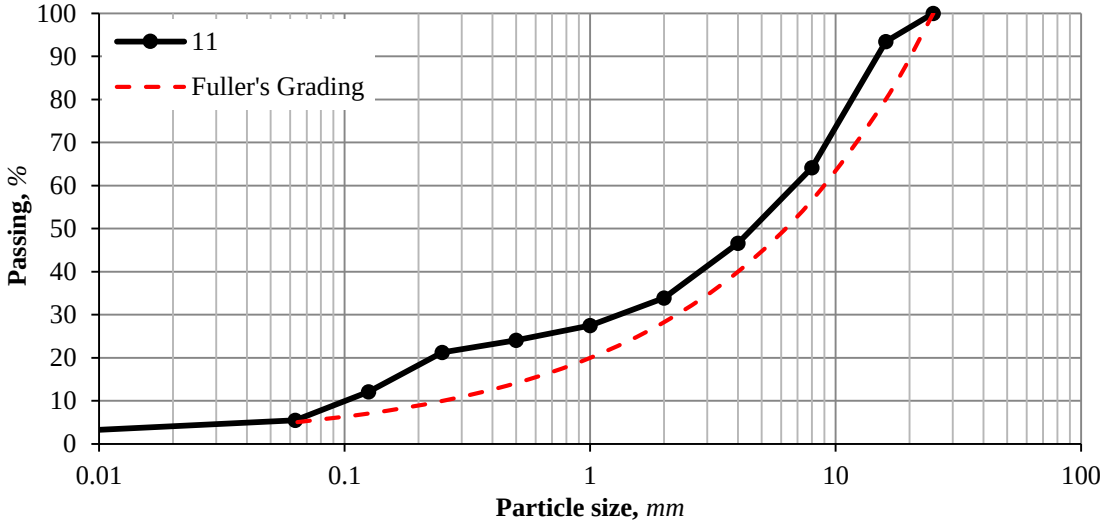

Figure 6-23 – Aggregate grading curve of sample 11

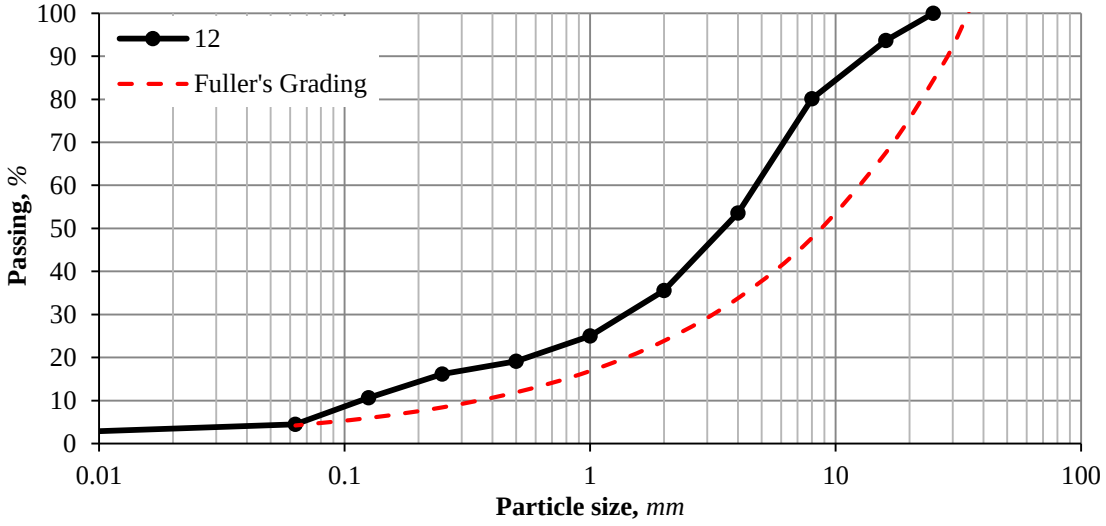

Figure 6-24 – Aggregate grading curve of sample 12

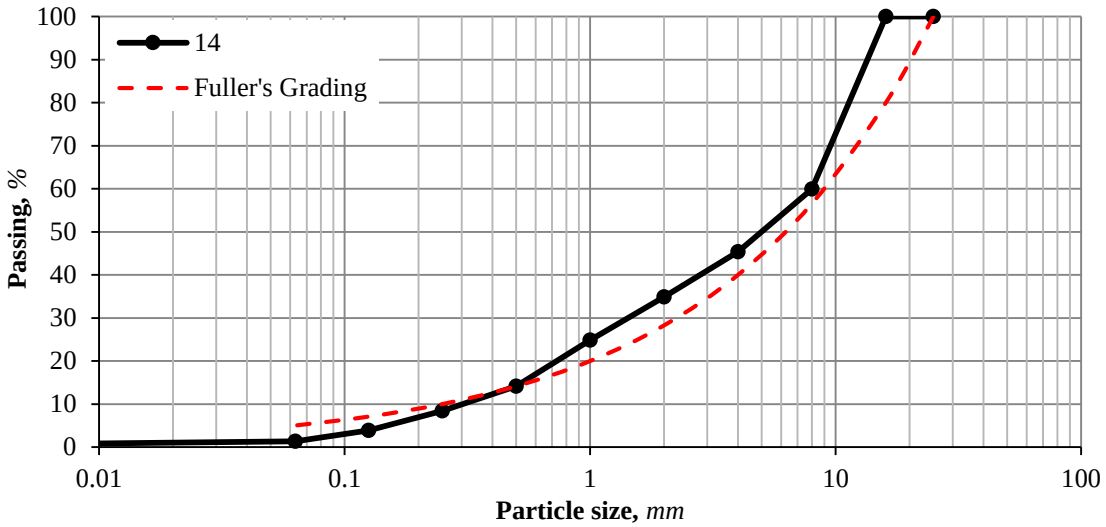

Figure 6-25 – Aggregate grading curve of sample 14

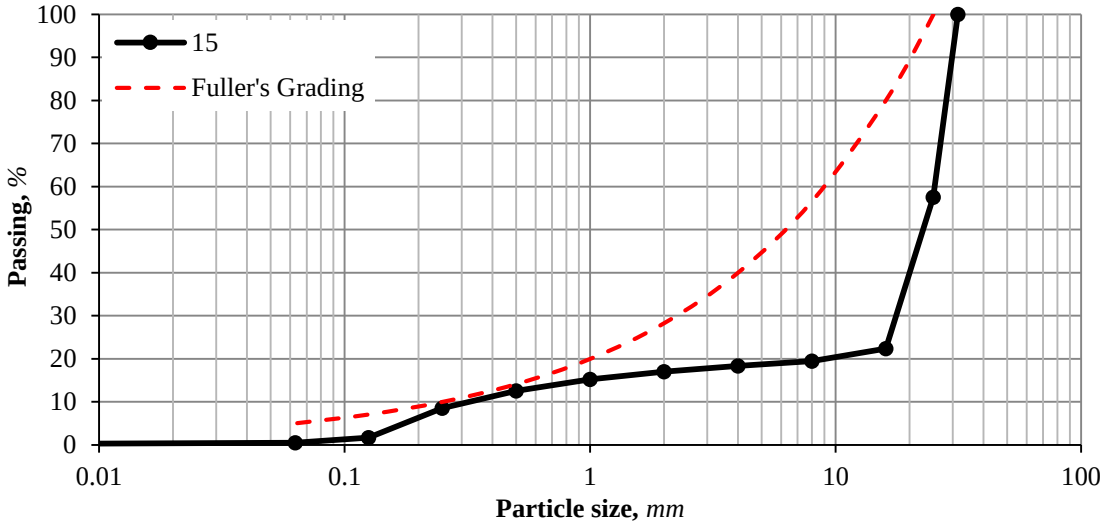

Figure 6-26 – Aggregate grading curve of sample 15

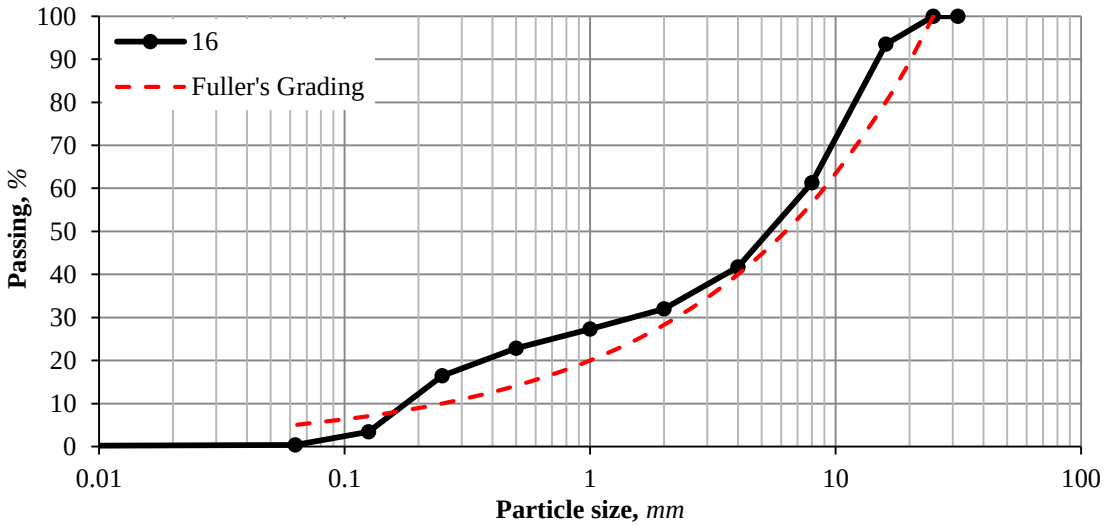

Figure 6-27 – Aggregate grading curve of sample 16

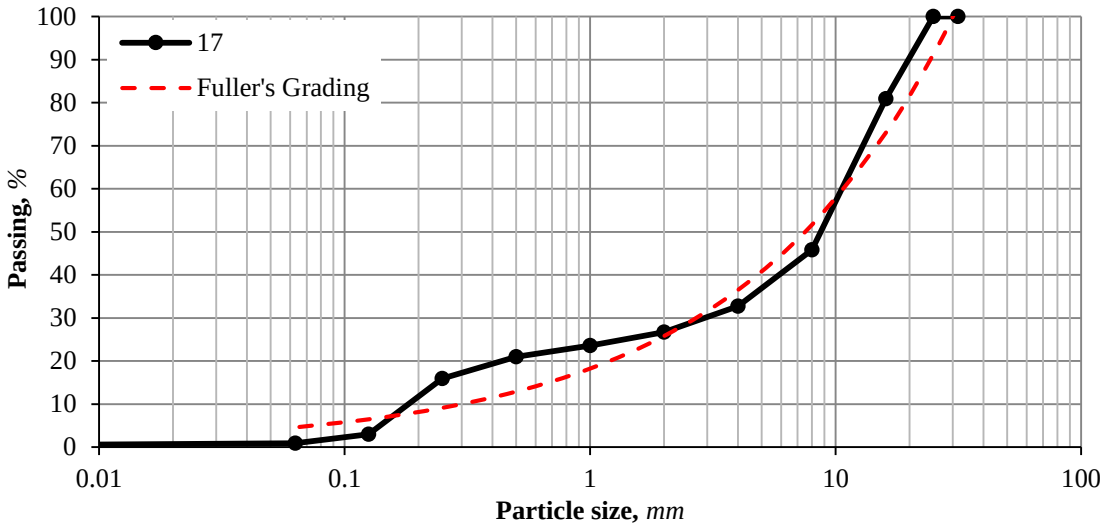

Figure 6-28 – Aggregate grading curve of sample 17

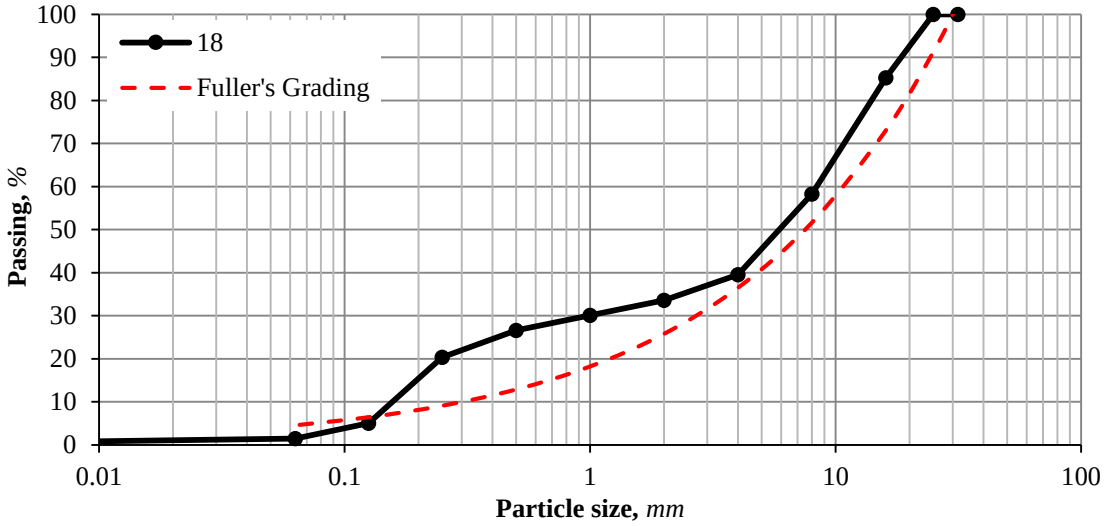

Figure 6-29 – Aggregate grading curve of sample 18

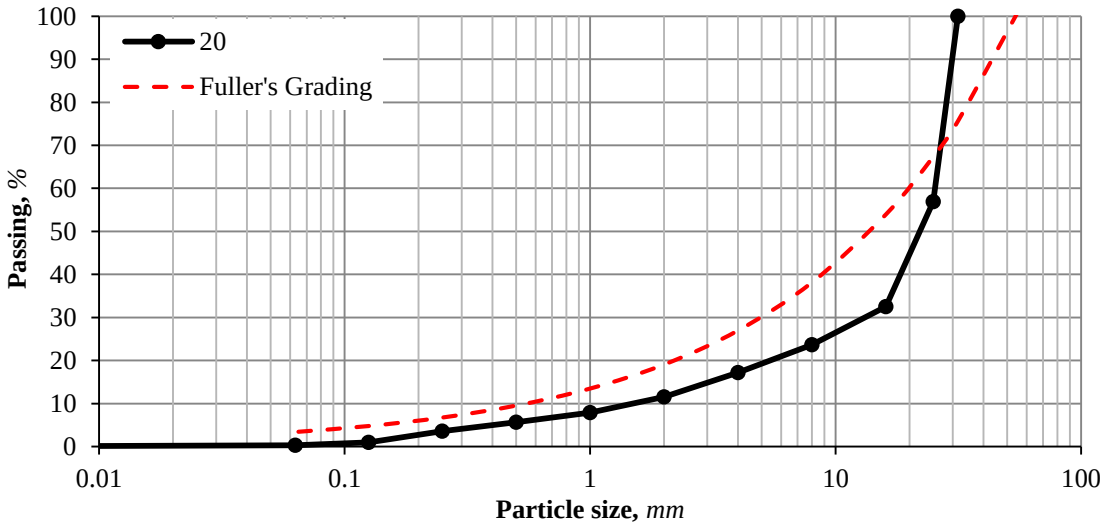

Figure 6-30 – Aggregate grading curve of sample 20

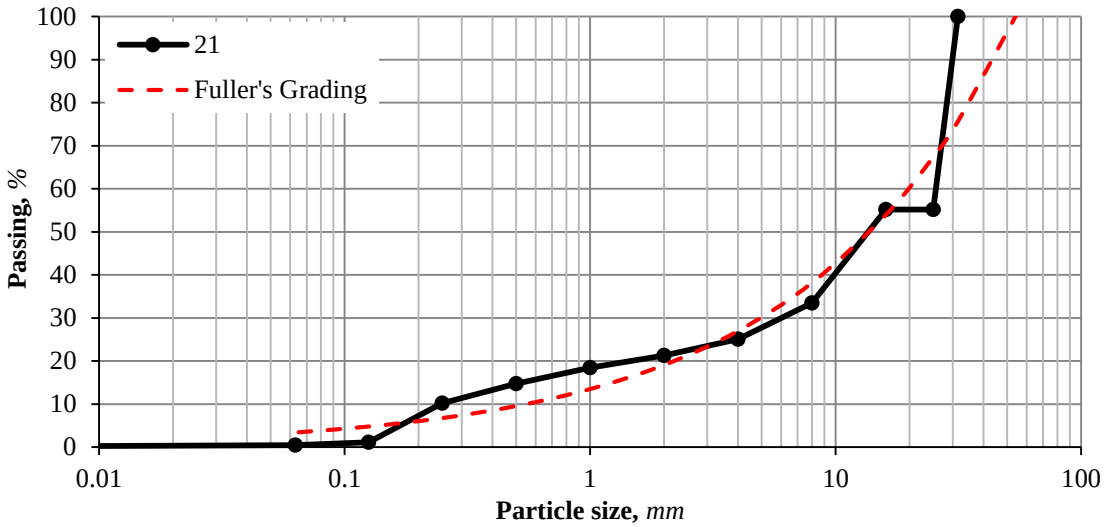

Figure 6-31 – Aggregate grading curve of sample 21

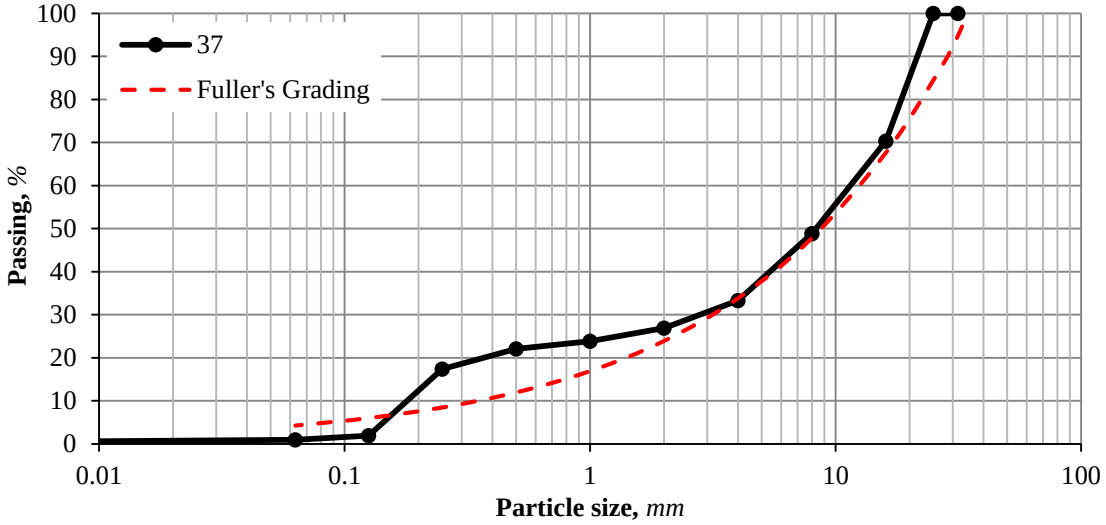

Figure 6-32 – Aggregate grading curve of sample 37

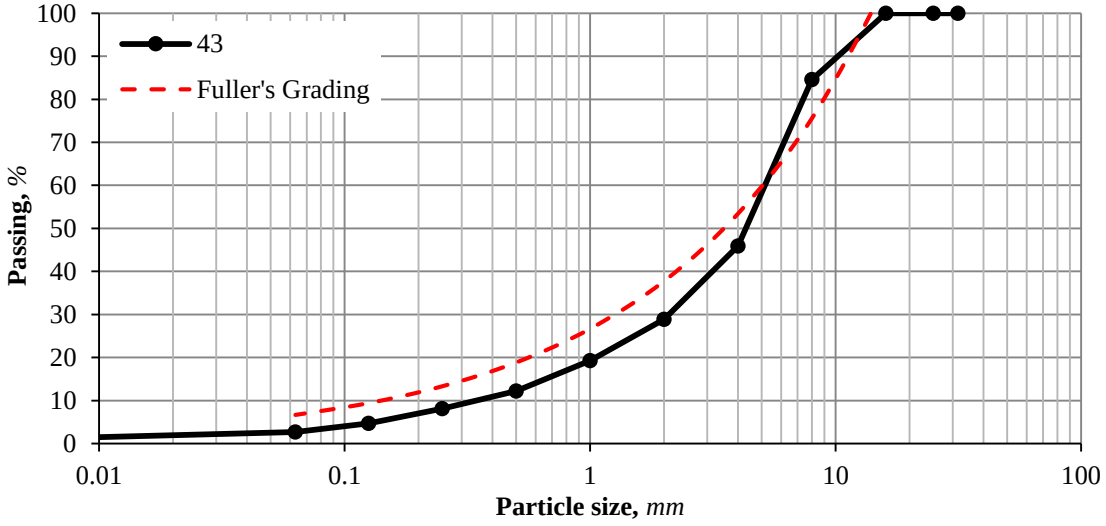

Figure 6-33 – Aggregate grading curve of sample 43

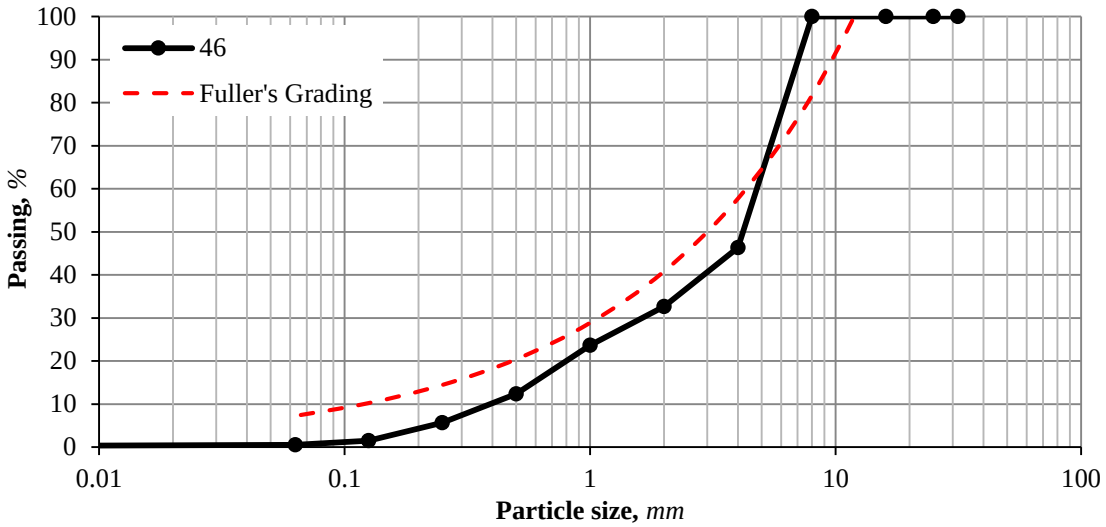

Figure 6-34 – Aggregate grading curve of sample 46

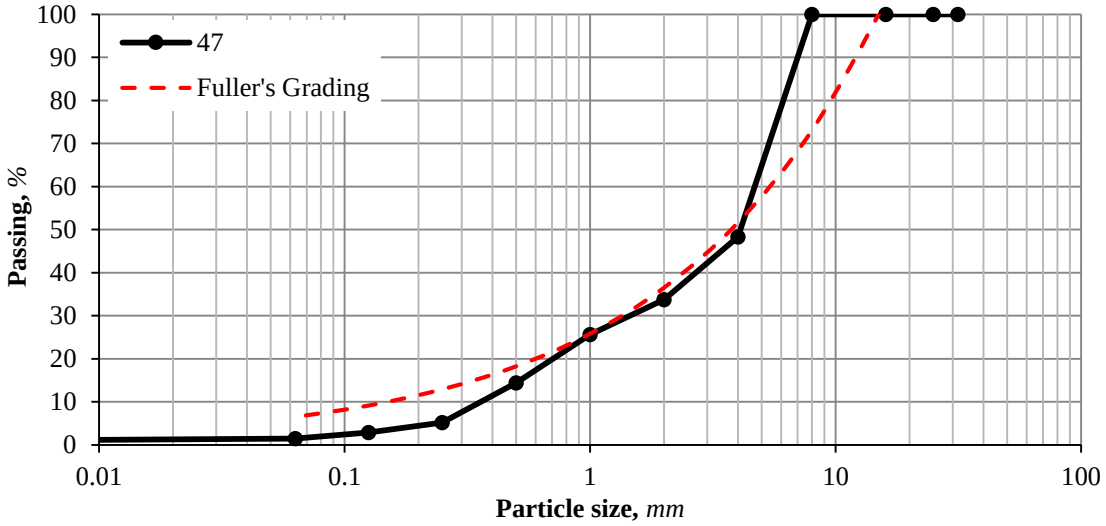

Figure 6-35 – Aggregate grading curve of sample 47

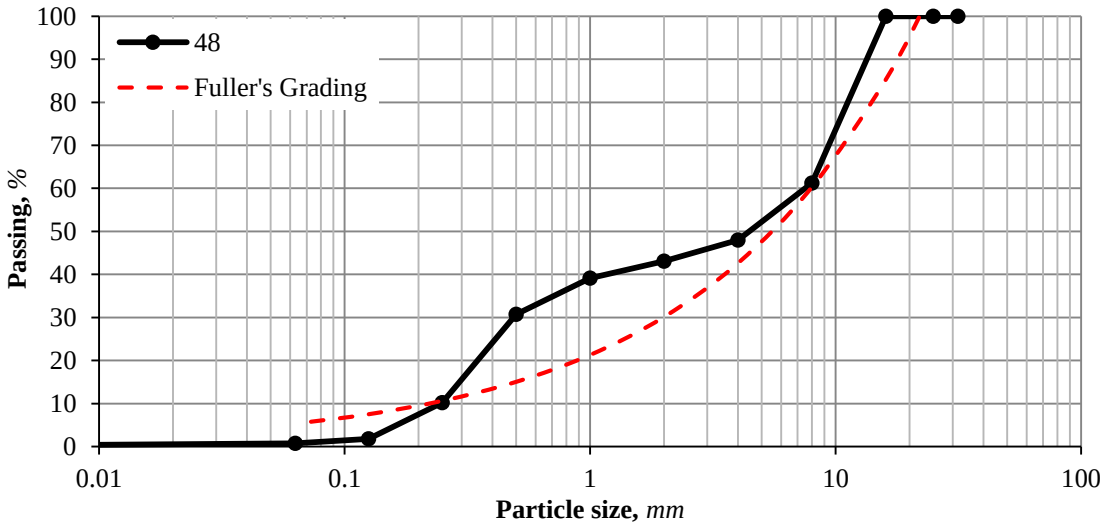

Figure 6-36 – Aggregate grading curve of sample 48

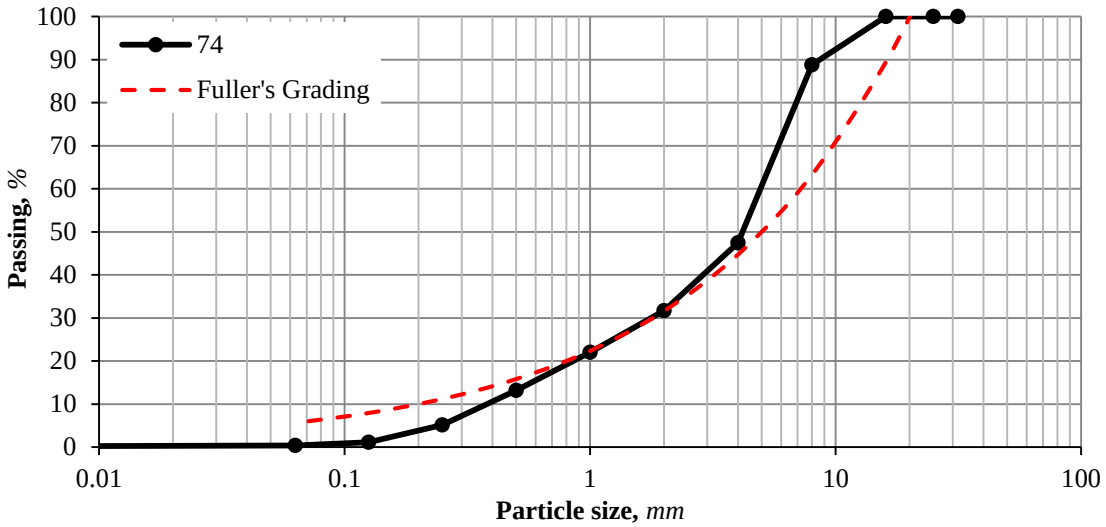

Figure 6-37 – Aggregate grading curve of sample 74

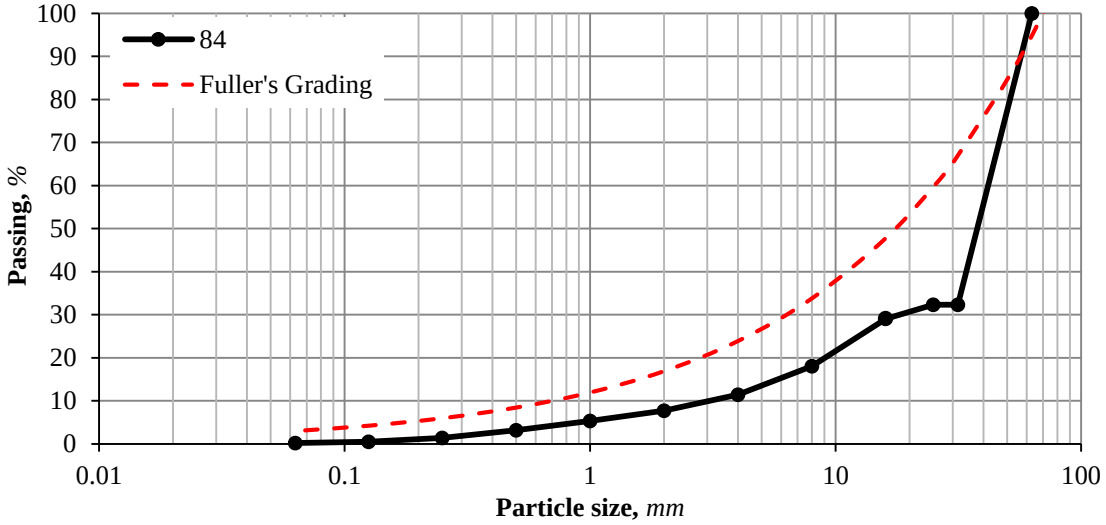

Figure 6-38 – Aggregate grading curve of sample 84

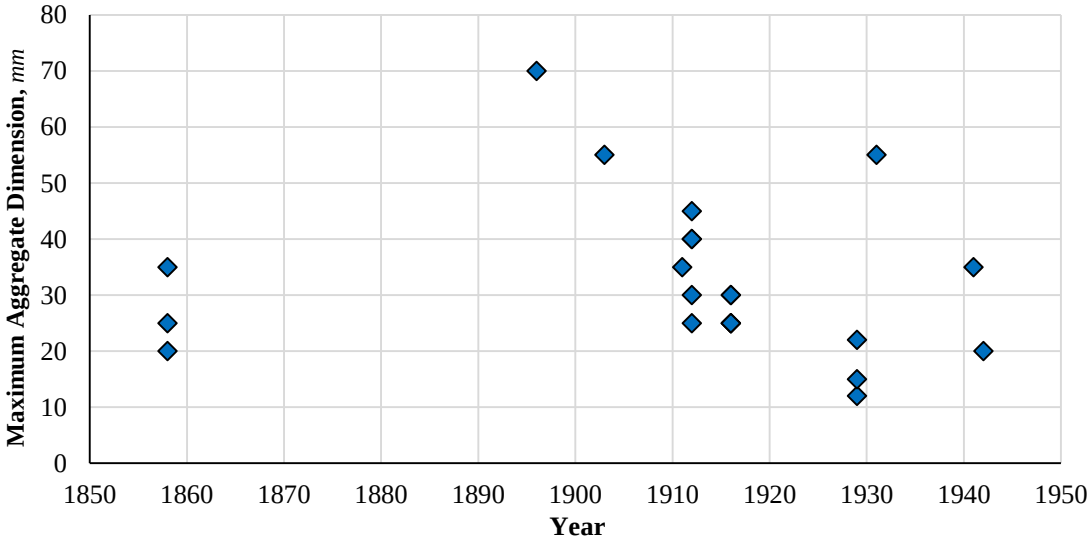

Figure 6-39 – Summary of maximum aggregate size by year

6.3.4.1 Discussion

The effects of maximum aggregate size and aggregate grading on the concrete mix have been discussed previously in Chapter 5.3.2.1 and 4.4.3, respectively. However, there has, so far, been no discussion on what constitutes as a 'good' grading.

At the start of the 20th Century, Fuller and Thompson (1907) carried out significant testing on concrete to determine how the grading of aggregates could be adjusted to provide the maximum workability and strength, with minimal segregation – the results of which were published in '*Transactions of the American Society of Civil Engineers'*. Subsequently, Talbot and Richart (1923) published the following equation, often referred to as 'Fuller's grading curve', for calculating 'optimum' aggregate grading:

$$P = 100 \times \left(\frac{d}{D}\right)^{n} \tag{49}$$

where:

P	is the percentage of material which passes a given sieve;
d	is the width of the sieve opening;
D	is the maximum size of particle of the given aggregate
n	is a variable component, with n = 0.5 resulting in the greatest density

While the idea of a universal optimum aggregate grading has long been abandoned – with the last aggregate grading limits in the UK published in, the now superseded, BS 882 (British Standards Institution, 1992) – the comparison to Fuller's grading curve can be useful in assessing aggregate grading to determine its likely effects on the properties of concrete. For example, a mix which has a large quantity of coarse aggregates can result in a mix which is harsh and unworkable (Mehta & Monteiro, 2006), difficult to finish (Neville & Brooks, 2010) and prone to segregation and honeycombing (Neville, 2011). Conversely, the use of very fine aggregates increases the water demand of the mix and, therefore, increases the cement content required to maintain a constant w/c ratio (Mehta & Monteiro, 2006).

As such, the effects of aggregate grading in historic concrete may have further significance with regards to its durability. When confronted with a concrete mix of low workability, the natural response is to add more water to the mix – thus increasing the workability, but also increasing the w/c. As previously discussed, increasing the w/c has

a significant impact on both the strength and durability of hardened concrete. Furthermore, as the relationship between w/c and durability has, historically, not been well understood – and alternatives such as superplasticisers did not exist – it is likely that additional mix water may have been added to mixes which had low workability due to the grading of aggregate.

In general, the samples analysed had a similar grading to the Fuller's grading curve calculated from their maximum aggregate size. However, Fuller & Thompson's research on the effects of aggregate grading was published in 1907, and, therefore, pre-dates the majority of the samples analysed in this study. As such, it is likely the industry was aware of their research and had some scientific understanding of the effects of aggregate grading.

Of the aggregate samples analysed, only five were cast prior to the publication of Fuller & Thompson's research: samples 10, 11 and 12 (1856-1859), sample 20 (1901-1905), and sample 84 (1896). Of these, both sample 20 and sample 84 had a large amount of very large particles and a deficiency in fine aggregate.

Figure 6-40 – Large air voids from poor compaction in Sample 84

With regards to maximum aggregate size, Figure 6-39 shows that there was a significant range of maximum aggregate sizes – as was the case for the samples discussed in Chapter 5.3.2.1. However, while the maximum aggregate sizes discussed in Chapter 5.3.2 were all from reinforced concrete structures, those discussed in this chapter came from a variety of concrete types – including reinforced concrete, mass concrete and precast concrete – which makes it more difficult to identify any trends in the results.

It should also be noted that, due to the lack of available material, all the aggregate samples analysed were from hardened concrete samples with approximate mass 0.3-0.5 kg – well below the 4 kg minimum specified in BS 1884-124 (British Standards Institution, 2015a). As such, it is possible that the calculated gradings are not a fully accurate representation of the bulk material.

Additionally, while it is conventional to consider the maximum aggregate size as the designated sieve aperture size on which 15% or more particles are retained, the maximum aggregate size reported and used for calculating Fuller's grading curve was the maximum measured aggregate dimension. This was done because there were many instances in which the maximum aggregate dimension was between the standard sieve sizes of 31.5 mm and 63 mm, which is too significant a range in size.

Table 6-35 – Summary of aggregate particle size analysis results

SAMPLE	AGE	MAXIMUM AGGREGATE SIZE	FINENESS MODULUS
03	1912	30	6.91
04	1912	45	7.55
05	1912	40	7.98
06	1911	35	7.41
08	1912	40	7.78
09	1912	25	6.92
10	1858	20	7.39
11	1858	25	6.71
12	1858	35	6.61
14	1916	25	7.07
15	1916	25	9.27
16	1916	25	7.01
17	1916	30	7.49
18	1916	30	7.00
20	1903	55	9.40
21	1931	55	8.65
37	1941	35	7.54
43	1978	14	6.94
46	1929	12	6.77
47	1929	15	6.68
48	1929	22	6.65
74	1942	20	6.90
84	1896	70	10.59

6.3.5 Drying Shrinkage

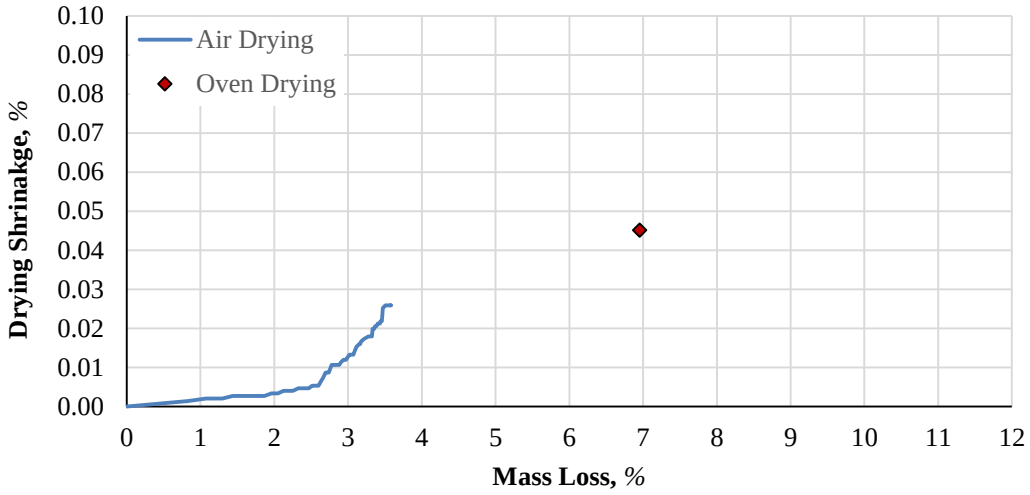

Figure 6-41 – Drying shrinkage of sample 03

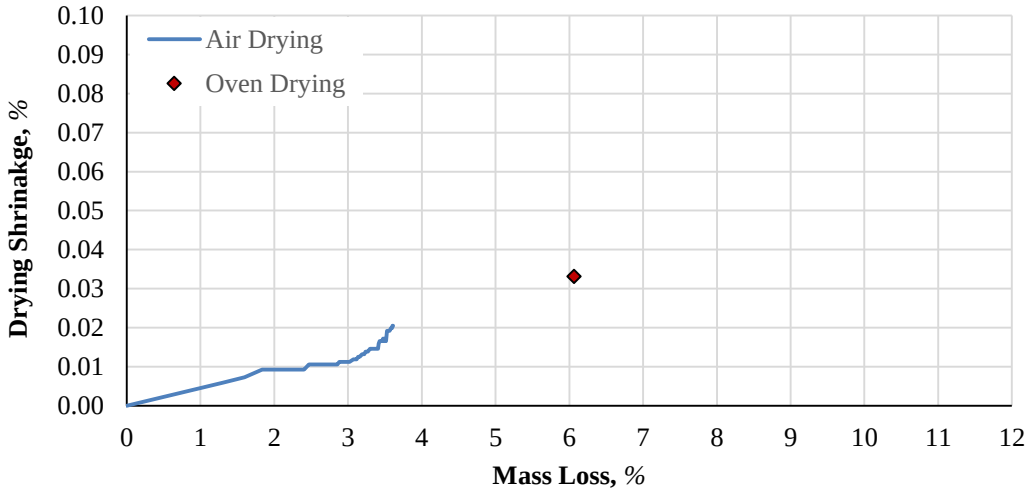

Figure 6-42 – Drying shrinkage of sample 04

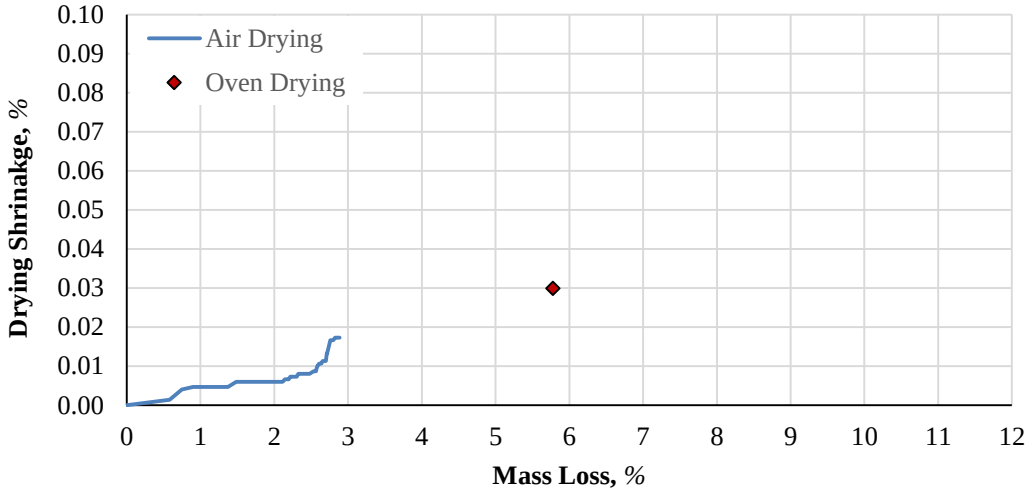

Figure 6-43 – Drying shrinkage of sample 05

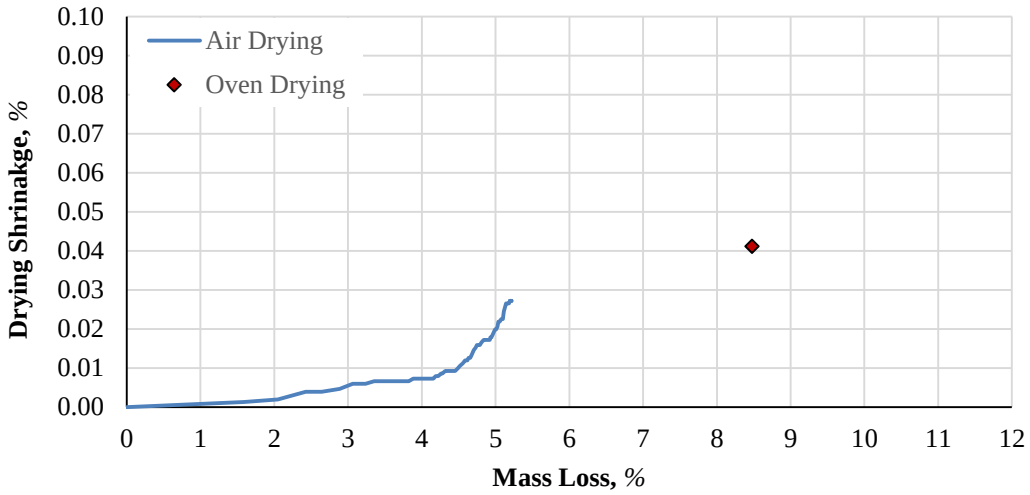

Figure 6-44 – Drying shrinkage of sample 06

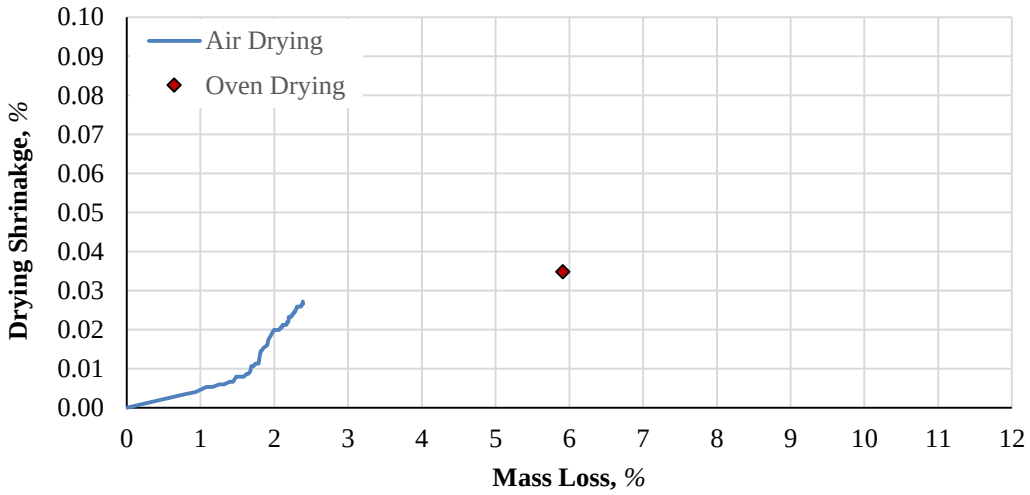

Figure 6-45 – Drying shrinkage of sample 08

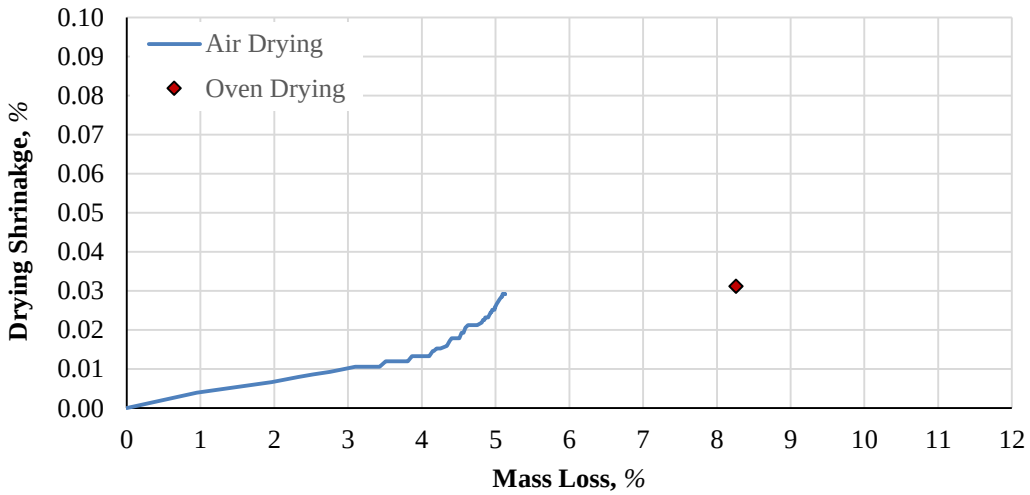

Figure 6-46 – Drying shrinkage of sample 09

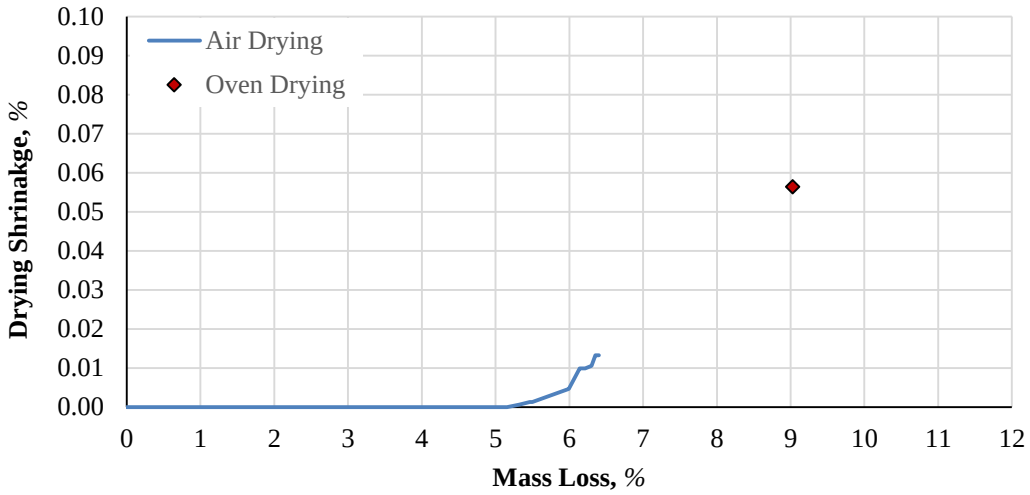

Figure 6-47 – Drying shrinkage of sample 10

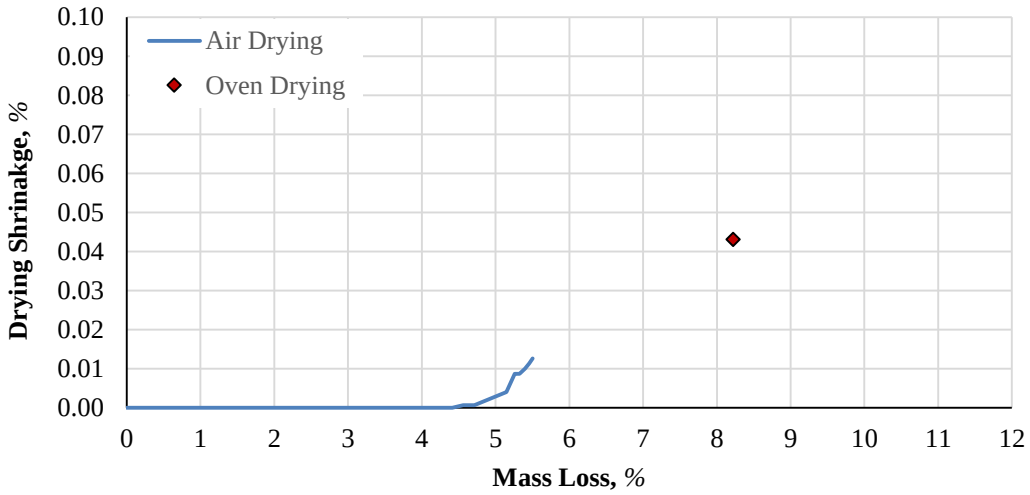

Figure 6-48 – Drying shrinkage of sample 11

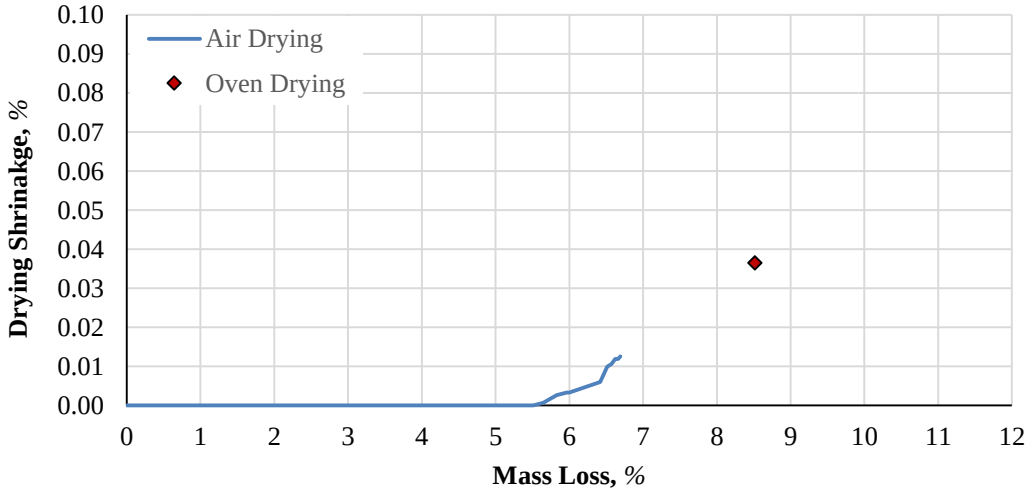

Figure 6-49 – Drying shrinkage of sample 12

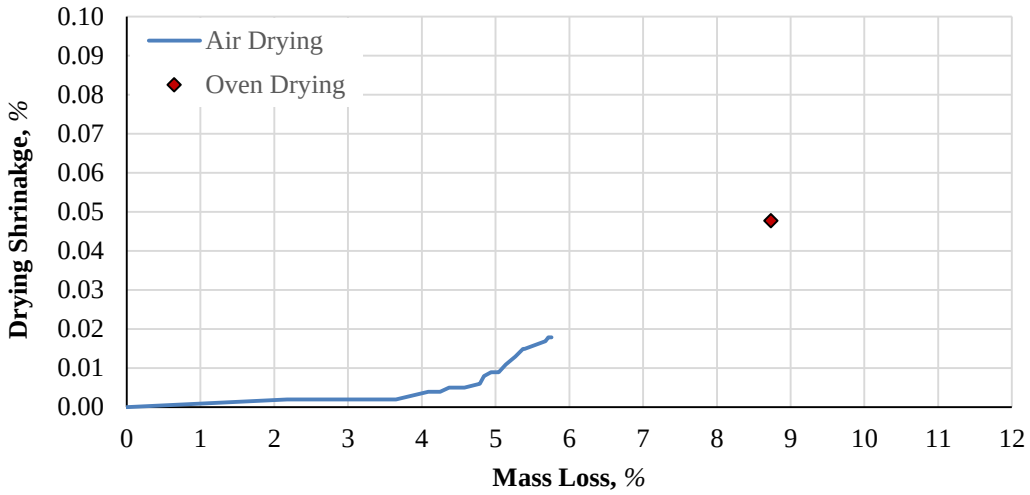

Figure 6-50 – Drying shrinkage of sample 13

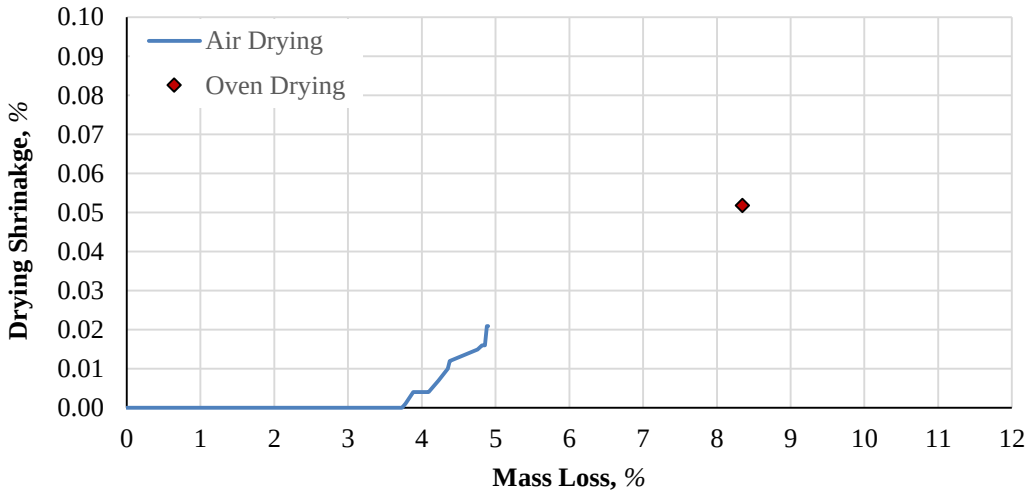

Figure 6-51 – Drying shrinkage of sample 14

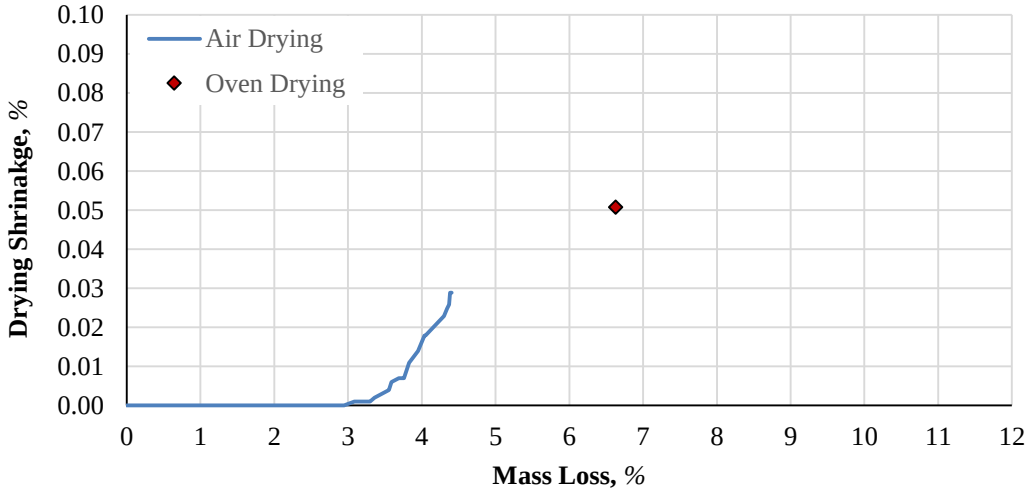

Figure 6-52 – Drying shrinkage of sample 15

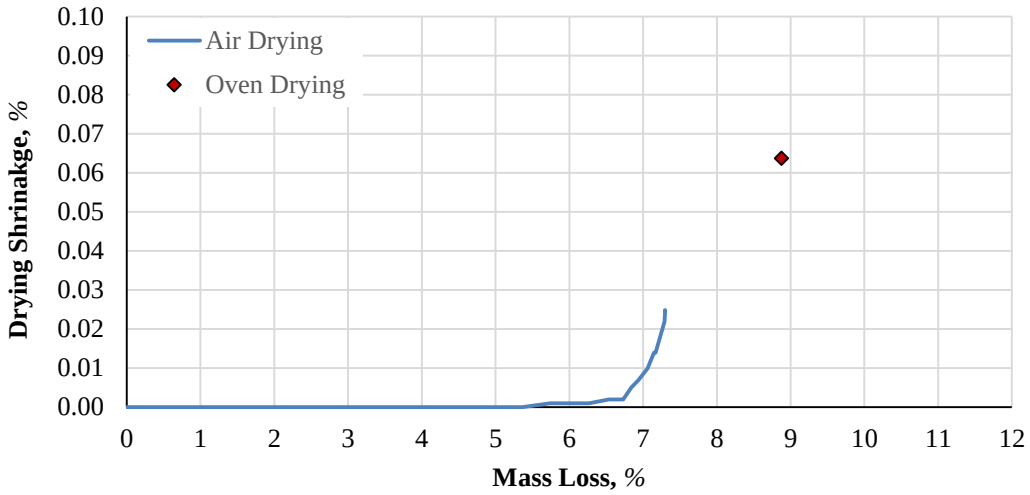

Figure 6-53 – Drying shrinkage of sample 16

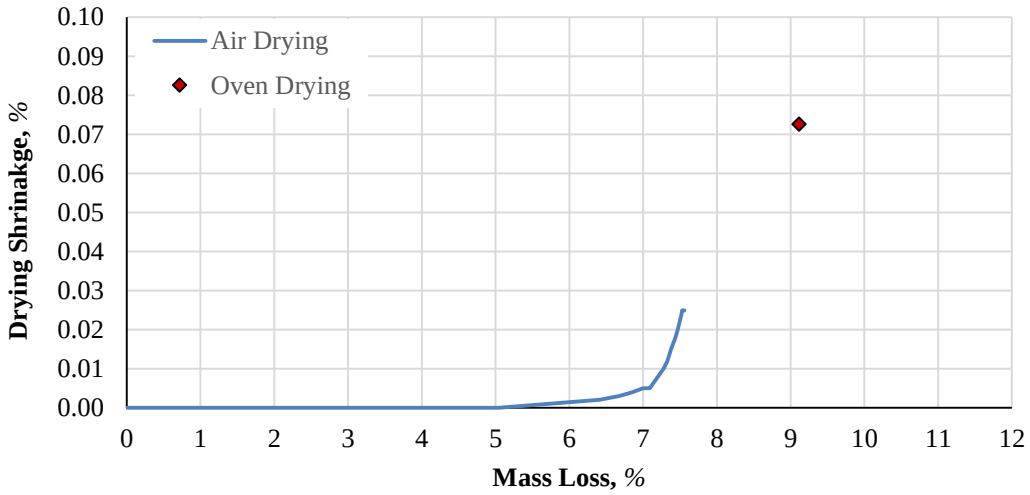

Figure 6-54 – Drying shrinkage of sample 17

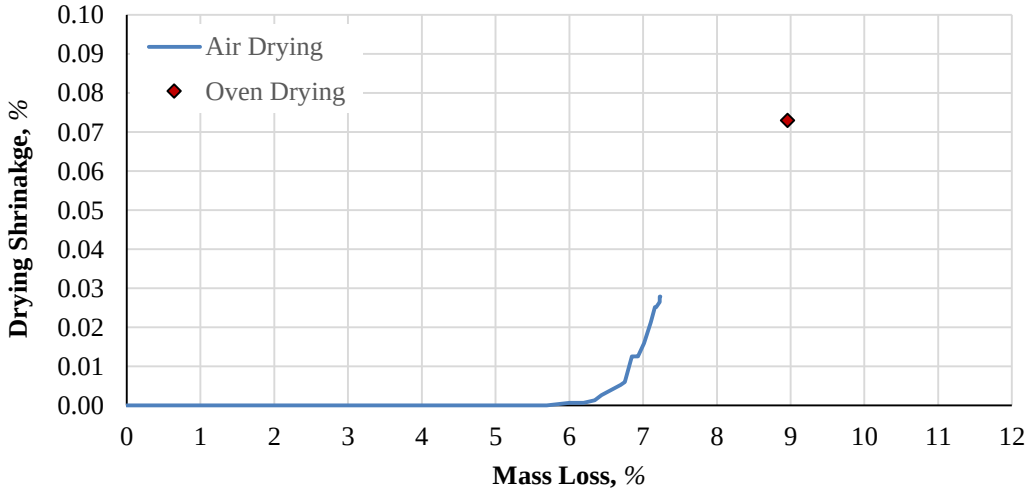

Figure 6-55 – Drying shrinkage of sample 18

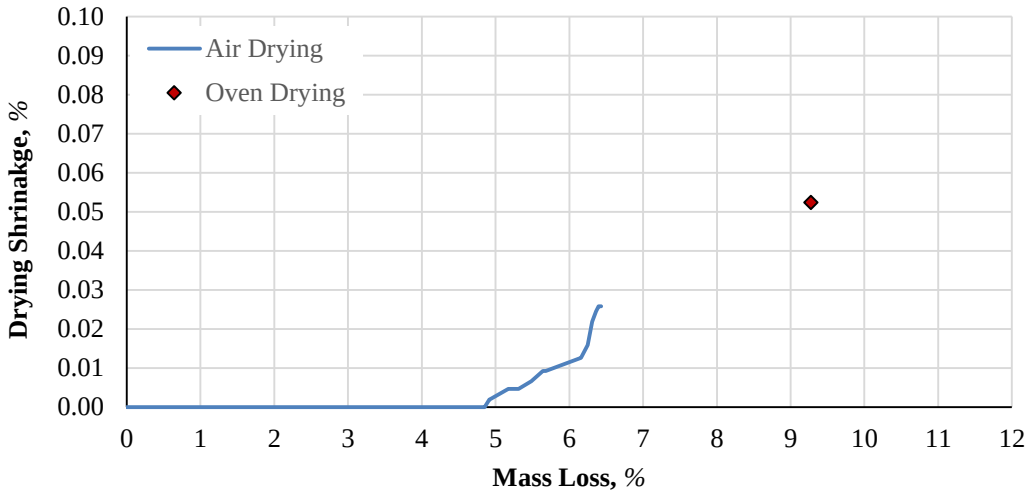

Figure 6-56 – Drying shrinkage of sample 20

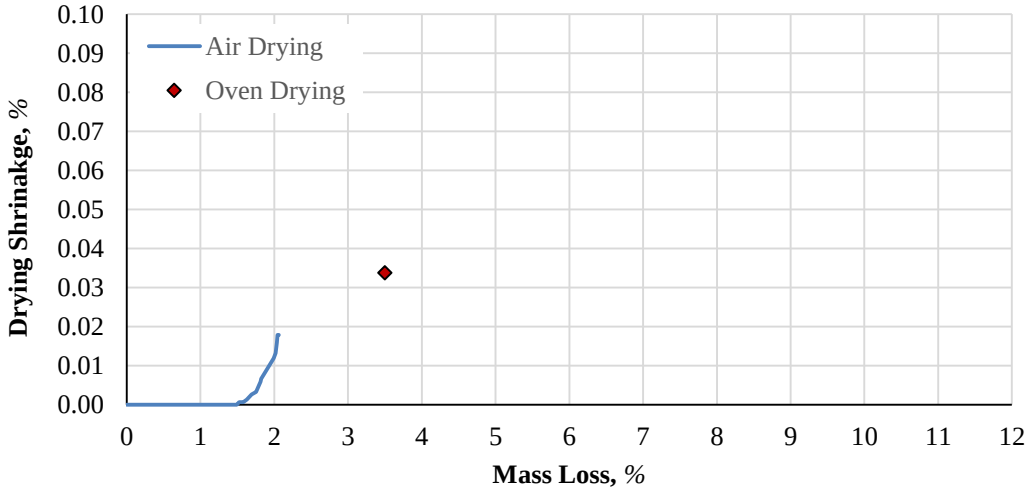

Figure 6-57 – Drying shrinkage of sample 21

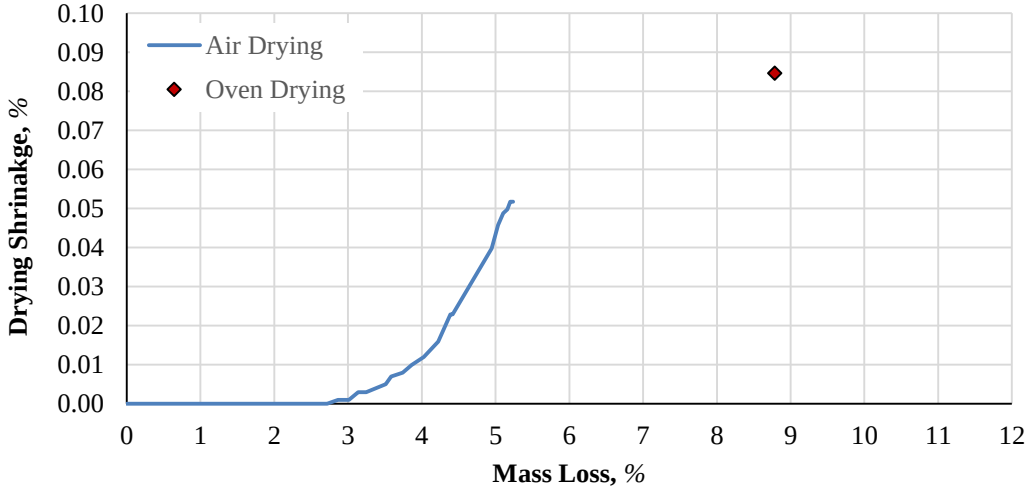

Figure 6-58– Drying shrinkage of sample 37

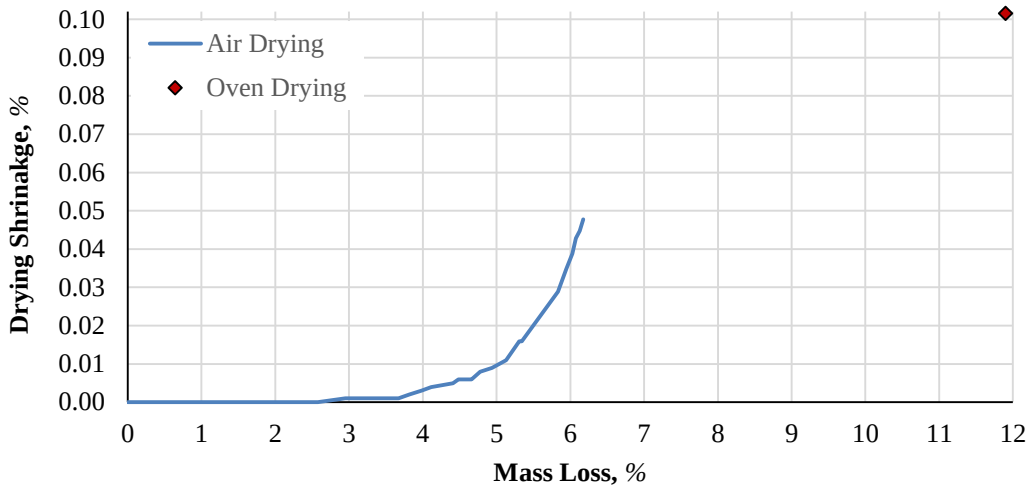

Figure 6-59 – Drying shrinkage of sample 43

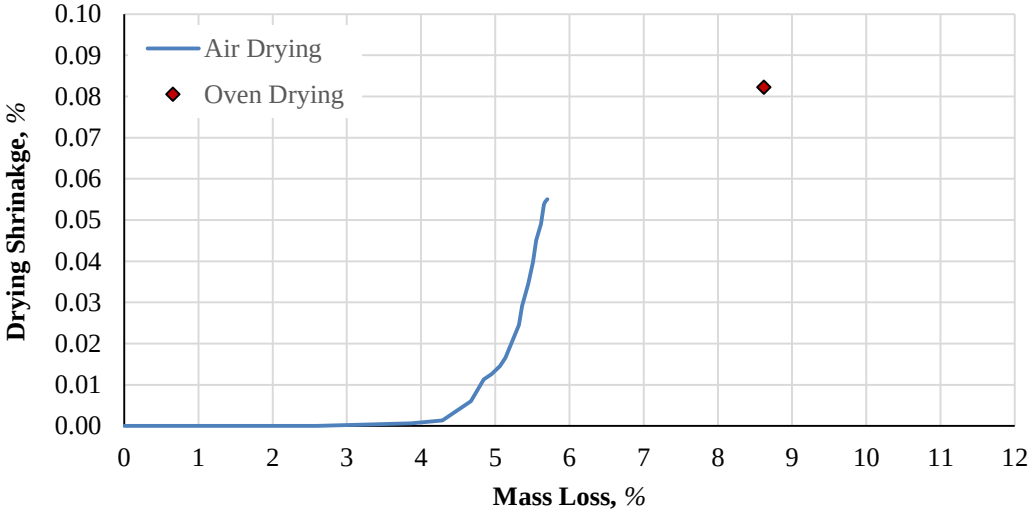

Figure 6-60 – Drying shrinkage of sample 46

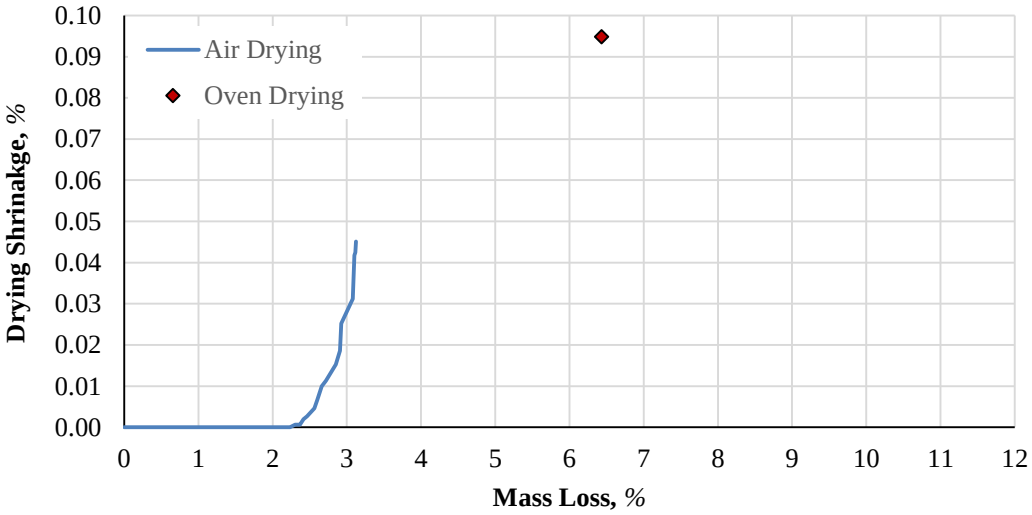

Figure 6-61 – Drying shrinkage of sample 47

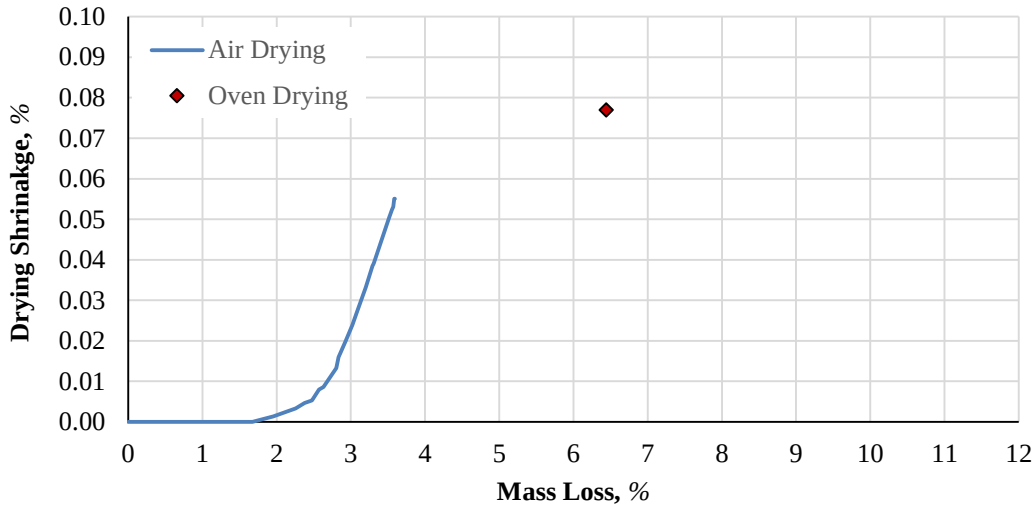

Figure 6-62 – Drying shrinkage of sample 48

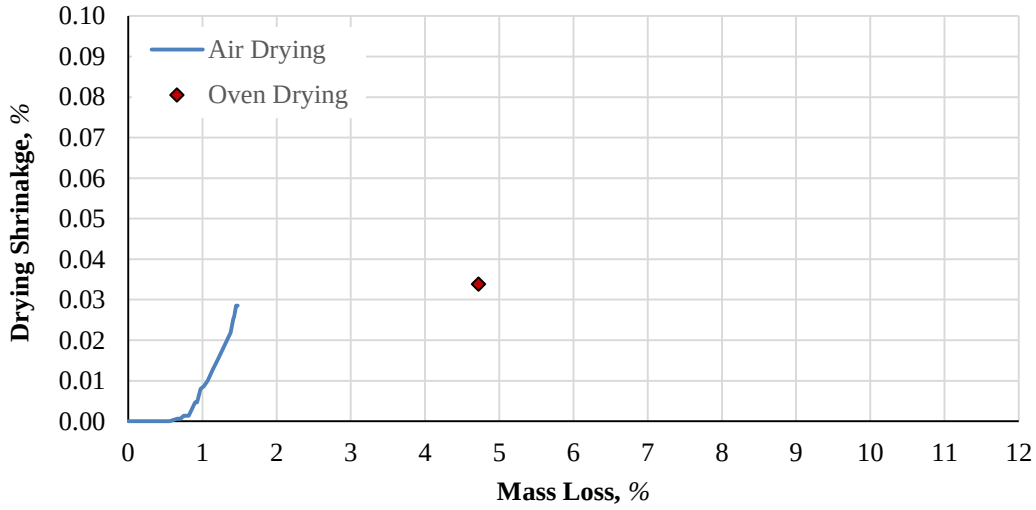

Figure 6-63 – Drying shrinkage of sample 74

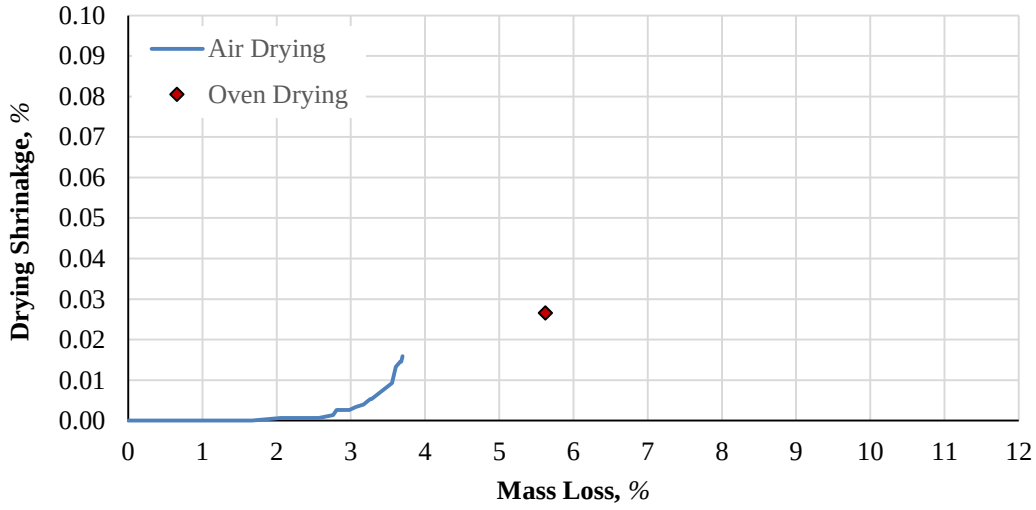

Figure 6-64 – Drying shrinkage of sample 84

6.3.5.1 Discussion

Drying shrinkage versus mass loss plots are shown for the various test specimens in Figure 6-41 to Figure 6-64. The shape of each of these plots can be divided into three distinct sections:

1. An initial section of mass loss, recorded during air-drying, during which very little or no shrinkage occurs;
2. A section, recorded during air-drying, showing an exponential increase in drying shrinkage with mass loss;
3. A final point of drying shrinkage recorded after oven-drying.

Each of these sections can be explained by examining the way in which water is stored in the concrete. As discussed in Chapter 2.6.1.1, drying shrinkage is the volumetric change of concrete due to moisture loss, but the change in volume of drying concrete is not equal to the total volume of water removed, as free water is also lost and this causes little or no shrinkage (Neville, 2011). The removal of free water – which occurred when the sample was removed from saturation and air-dried at a controlled temperature and humidity – is shown in the first section of each plot, where a relatively large percentage of mass is lost with little or no shrinkage occurring.

The second section of each plot represents the period of air-drying during which the water that is held in the larger capillary pores – described in Table 2-7 – is lost to the surrounding air, and drying shrinkage occurs until equilibrium is reached and no more water is lost. An example of this equilibrium can be clearly seen in the mass loss plot shown in Figure 6-65.

The final point of each plot represents the period of oven-drying, during which a significant mass of water was removed. This water is the remaining water that is trapped in the smaller gel pores but diffuses out of the concrete during heating – resulting in significant shrinkage.

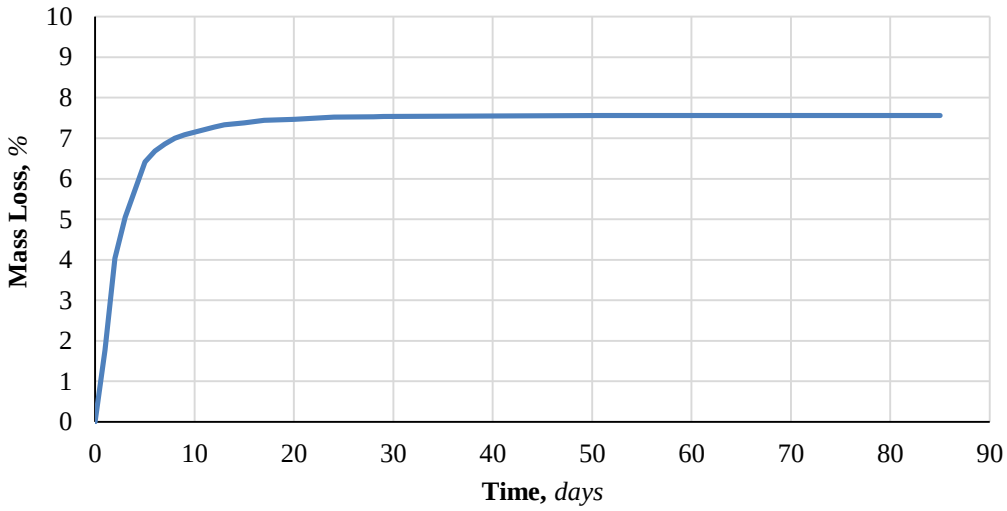

Figure 6-65 – Example of mass loss against time during air-drying

There are several factors which may affect the extent of drying shrinkage which occurs in concrete specimens – many of which were discussed in Chapter 2.6.1. In order to determine which of these variables affects shrinkage, best subset regression and factor analyses were carried out. The input data for these analyses can be found in Table 6-36, the results of best subset regression in Table 6-37, and the loading plots from the factor analyses in Figure 6-66 to Figure 6-69.

In the subsequent discussion, the ratio of 'surface area/volume' is referred to as 'SA/V', and the variable 'porosity' considers the entire concrete specimen and was calculated using the saturated and oven-dry density results – previously referred to as 'concrete voids ratio' in Chapter 4.3.1.6.

Variables Influencing Drying Shrinkage

From the results of best subset regression, it would appear that the individual variable which most influences the ultimate shrinkage (oven-dried), is the density of the samples. However, this model is fairly inaccurate and a more accurate model for predicting the ultimate shrinkage can be determined by examining the subset models which contain more variables.

Taking into consideration the R^2 adjusted values only, it would appear that subset 1G best explains the variation of ultimate drying shrinkage. Subset 1G also has the lowest S (standard error) value – indicating that it is also the most accurate of the models. However, the Mallows' Cp value is relatively low in comparison to the number of

parameters considered, which indicates it may not be as precise as other models, when compared to the full model.

In consideration of R^2 adjusted, subsets 1I and 1J have the next highest values – and also have relatively low S values. However, they each consider 5 out of the 8 possible variables, and so the possibility of overfitting needs to be considered. Overfitting occurs when the regression considers traits that are unique to the samples considered in the regression as being valid predictors for all future responses.

In this case, the variable 'volume' stands out as a source of overfitting. Only a limited number of samples provided for this project were suitable for use in the drying shrinkage study due to their physical dimensions, and several of those that were suitable came from the same source and had the same dimensions. For example, samples 3-9 were cores (80×150 mm) from Arklet Dam, and samples 10-12 were cores (120×150 mm) from Loch Katrine. As such, it is possible that the regression model is incorrectly considering a correlation between specimen volume and other variables which are inherent to the source of the concrete.

This hypothesis can be considered further by examining the results of the factor analysis. In all four of the factor loading diagrams, 'ultimate strain' and 'volume' are close to 90° apart from each other which suggests no correlation between the ultimate shrinkage and the volume of the specimen – supporting the theory that the inclusion of volume in the best subset regression models may be a result of overfitting. Similarly, the variable 'SA/V' appears to show very little correlation to ultimate strain in any of the rotated loading plots, and so its inclusion in best subset models in response to ultimate strain is also probably a result of overfitting – although, while SA/V does not appear to affect ultimate shrinkage, it did have a significant effect on the rate of drying shrinkage due to an increase in the rate of moisture loss.

Furthermore, the lack of correlation between either of these variables and ultimate strain also concurs with research carried out by Almudaiheem & Hansen (1987), which suggested that ultimate drying shrinkage of concrete, mortar and cement paste was independent of specimen size and shape.

This method of analysis can also be applied to other variables considered in the best subset regression. For example, the relatively small angles between 'mass loss' and 'ultimate shrinkage' in each of the rotated loading plots suggests quite a strong correlation between

these two variables. The variables 'oven-dry density' and 'aggregate content' similarly are separated by a relatively small angle, and so a strong correlation between these two variables is also implied. Furthermore, both of these variable are separated from 'ultimate shrinkage' by almost 180°, which in turn suggests a strong anti-correlation between each of these two variables and ultimate shrinkage – i.e. as either oven-dry density or aggregate content increases, the ultimate shrinkage decreases.

Each factor loading plot also suggests a strong correlation between 'maximum aggregate size' and 'fineness modulus'. This is to be expected as the fineness modulus (FM) is the sum of the cumulative percentages *retained* on the sieves of the standard series divided by 100, and, therefore, samples containing larger aggregates size have a FM value. Furthermore, the factor loading plot with no rotation suggest a very strong anti-correlation between the both of variables, 'maximum aggregate size' and 'fineness modulus', with 'ultimate shrinkage'. However, this anti-correlation, while still present, is less pronounced in each of the various rotated loadings.

Taking into account the results from the factor analysis, the results of the best subset regression need to be reconsidered and, if ultimate shrinkage is considered independent of both SA/V and volume, then subset models including these terms should be considered to be the result of overfitting and disregarded. As such, it would appear that the best subset model is 1E which indicates that the most important variables affecting ultimate shrinkage are oven-dry density, maximum aggregate size and aggregate content – variables which all have a strong anti-correlation with ultimate shrinkage according to the factor analysis.

The influence of aggregate on drying shrinkage was discussed in Chapter 2.6.1.1, and the relationship between these variables and ultimate shrinkage can be understood from this discussion. As discussed in Chapter 2.6.1.1, the majority of drying shrinkage is attributed to the cement paste and the effect of aggregate content is twofold: Firstly, as aggregate is generally more dense and has a lower shrinkage capacity, increasing the aggregate content results in a decrease in the overall shrinkage of concrete, and also results in an increase in density – thus explaining the relationship between aggregate content, oven-dried density and ultimate shrinkage. Secondly, the use of aggregate reduces the shrinkage of concrete by providing internal restraint (Imamoto & Arai, 2008), and it would seem from this analysis that the size of the aggregate has an effect on the extent of this – with larger aggregates providing greater restraint.

Table 6-36 – Data used in first multivariate analysis

SAMPLE	ULTIMATE SHRINKAGE	MASS LOSS	MAX. AGGREGATE	FINENESS MODULUS	AGGREGATE CONTENT	SURFACE AREA/VOLUME	VOLUME	OVEN-DRY DENSITY	POROSITY
	%	%	mm	–	%	m^{-1}	m^3	kg/m^3	%
03	0.045	7.0	30	6.91	70.9	66.2	0.00076	2193	18.1
04	0.033	6.1	45	7.55	80.2	66.6	0.00076	2282	14.4
05	0.030	5.8	40	7.98	67.9	66.7	0.00075	2286	14.2
06	0.041	8.5	35	7.41	72.1	66.0	0.00076	2147	19.7
08	0.035	5.9	40	7.78	69.4	60.9	0.00081	2237	15.2
09	0.031	8.3	25	6.92	60.5	60.3	0.00083	2337	6.4
10	0.056	9.0	20	7.39	64.7	47.1	0.00162	2074	20.6
11	0.043	8.2	25	6.71	68.0	46.6	0.00166	2118	19.0
12	0.036	8.5	35	6.61	65.3	46.9	0.00165	2068	19.3
14	0.052	8.3	25	7.07	46.0	87.6	0.00067	2104	19.2
15	0.051	6.6	25	9.27	74.5	145.9	0.00083	2221	15.8
16	0.064	8.9	25	7.01	71.2	70.5	0.00120	2089	20.4
17	0.073	9.1	30	7.49	70.4	108.6	0.00044	2076	20.9
18	0.073	9.0	30	7.00	70.1	80.0	0.00121	2077	20.5
20	0.052	9.3	55	9.40	74.4	58.1	0.00103	2037	20.9
21	0.034	3.5	55	8.65	82.2	62.1	0.00077	2372	8.6
37	0.085	8.8	35	7.54	71.0	75.4	0.00057	2057	19.9
43	0.101	11.9	14	6.94	54.4	72.8	0.00060	1581	21.4
46	0.082	8.6	12	6.77	84.5	70.2	0.00075	1966	18.6
47	0.095	6.4	15	6.68	83.8	68.5	0.00080	2103	14.5
48	0.077	6.4	22	6.65	70.2	68.2	0.00077	2193	14.5
74	0.034	4.7	20	6.90	68.7	64.3	0.00086	2184	10.8
84	0.027	5.6	70	10.59	76.8	49.0	0.00152	2379	14.2

Table 6-37 – Results of first 'best subset regression' for response 'ultimate shrinkage'

Subset	No. Variable	R^2	R^2 Adjusted	Cp	S	Mass Loss	Max. Agg. Size	Fineness Modulus	Agg. Content	SA/V	Volume	Oven-Dry Density	Porosity
1A	1	55.6	53.5	5.6	0.015337							x	
1B	1	34.0	30.8	17.6	0.018709		x						
1C	2	63.2	59.5	3.4	0.014310				x			x	
1D	2	61.6	57.7	4.3	0.014627						x	x	
1E	3	69.4	64.5	2.0	0.013402		x		x			x	
1F	3	68.6	63.6	2.4	0.013566				x		x	x	
1G	4	73.2	67.2	1.8	0.012878		x		x		x	x	
1H	4	72.1	65.9	2.4	0.013129		x		x	x		x	
1I	5	74.1	66.5	3.3	0.013023	x	x		x		x	x	
1J	5	74.0	66.3	3.4	0.013054		x		x		x	x	x
1K	6	74.5	65.0	5.1	0.013312	x	x		x	x	x	x	
1L	6	74.4	64.8	5.2	0.013348	x	x		x		x	x	x
1M	7	74.7	62.9	7.0	0.013707	x	x	x	x		x	x	x
1N	7	74.6	62.8	7.0	0.013719	x	x		x	x	x	x	x
1O	8	74.7	60.3	9.0	0.014181	x	x	x	x	x	x	x	x

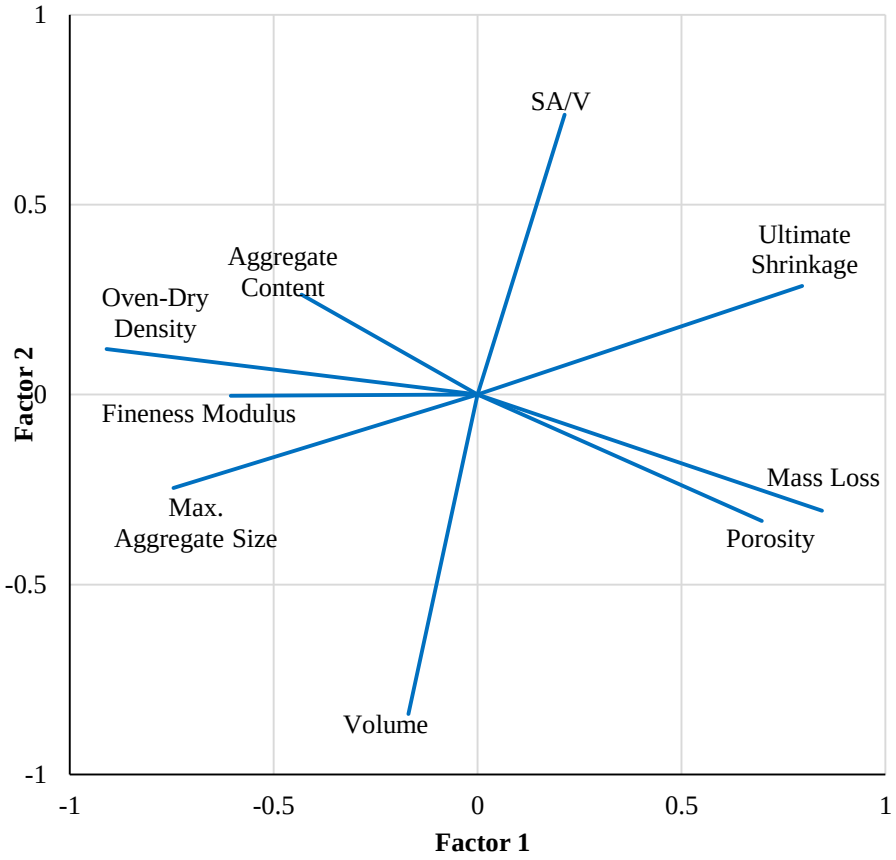

Figure 6-66 – Factor loading plot, analysis 1 (no rotation)

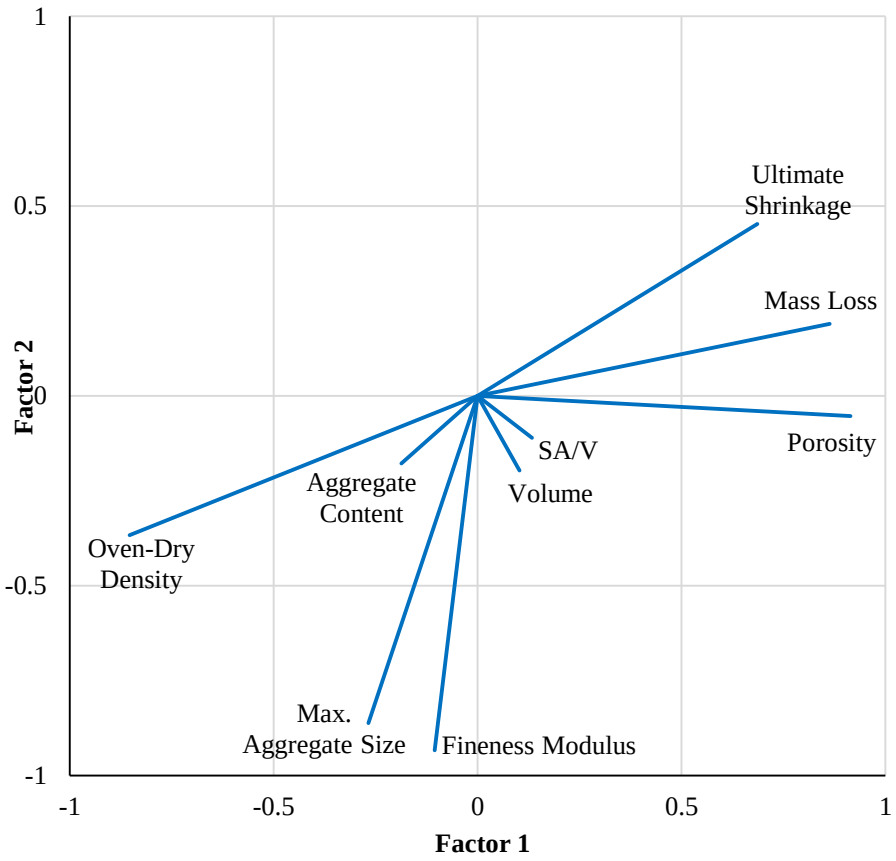

Figure 6-67 – Factor loading plot, analysis 1 (Varimax rotation)

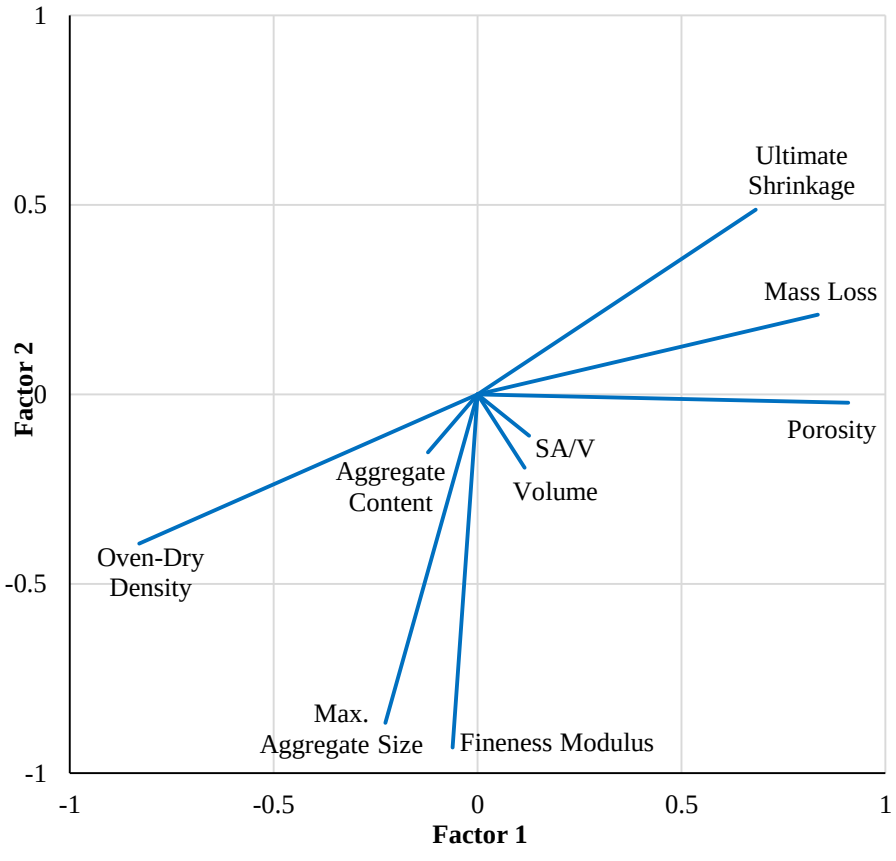

Figure 6-68 – Factor loading plot, analysis 1 (Equimax rotation)

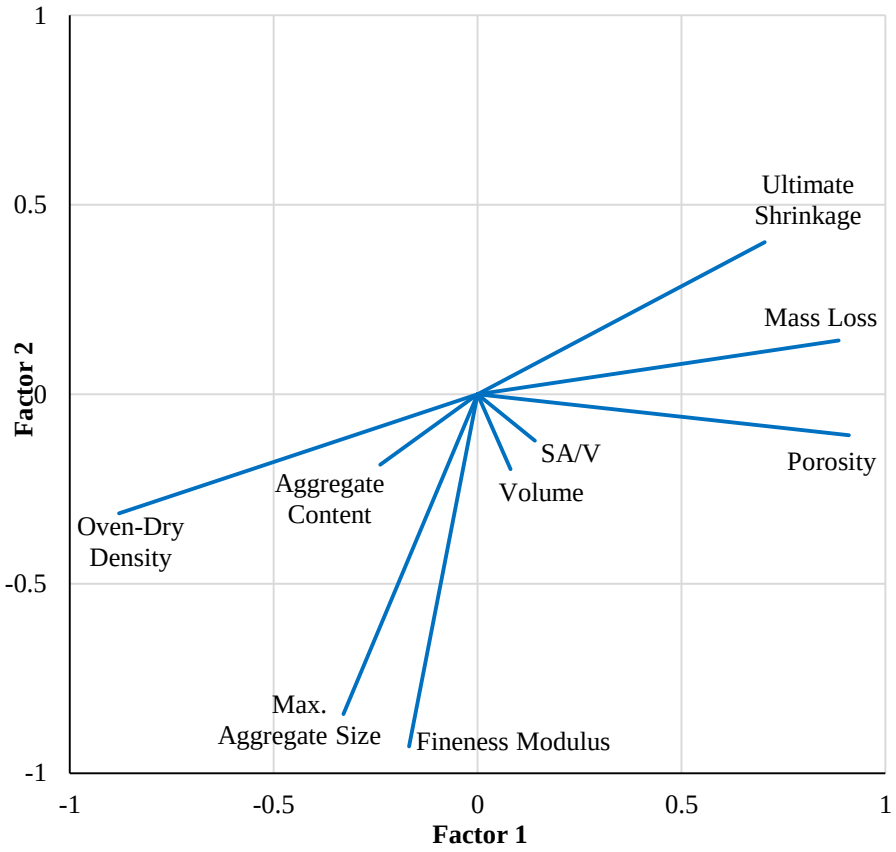

Figure 6-69 – Factor loading plot, analysis 1 (Quartimax rotation)

Determining Ultimate Shrinkage

If best subset model is considered to be 1E – with the most important variables affecting ultimate shrinkage being oven-dry density, maximum aggregate size and aggregate content – the regression equation for ultimate shrinkage, with standard error of 0.0134, is:

$$US = 0.213 + 0.000832 \times AC - 0.000094 \times ODD - 0.000470 \times MAS \qquad (50)$$

where:

US is ultimate shrinkage, as a percentage;
AC is aggregate content, as a percentage;
ODD is oven-dry density, in kg/m^3;
MAS is maximum aggregate size, in mm.

Using this equation, a prediction of ultimate was calculated for each sample and compared to the actual ultimate shrinkage observed during the experimental procedure, as shown in Table 6-38:

Table 6-38 – Comparison between actual shrinkage observed and shrinkage prediction 1

SAMPLE	ULTIMATE SHRINKAGE OBSERVED	ULIMATE SHRINKAGE PREDICTED	ERROR
3	0.045	0.052	0.007
4	0.033	0.044	0.011
5	0.030	0.036	0.006
6	0.041	0.055	0.014
8	0.035	0.042	0.007
9	0.031	0.032	0.001
10	0.056	0.062	0.006
11	0.043	0.059	0.016
12	0.036	0.057	0.021
14	0.052	0.042	-0.010
15	0.051	0.055	0.004
16	0.064	0.064	0.000
17	0.073	0.062	-0.011
18	0.073	0.062	-0.011
20	0.052	0.058	0.006
21	0.034	0.032	-0.002
37	0.085	0.062	-0.023
43	0.101	0.103	0.002
46	0.082	0.093	0.011
47	0.095	0.078	-0.017
48	0.077	0.055	-0.022
74	0.034	0.055	0.021
84	0.027	0.020	-0.007

However, these predictions of ultimate shrinkage do not take into consideration the effects that chemical composition of the binder will have on the shrinkage properties of the concrete. As discussed in Chapter 2.2.1, the chemical composition of cement determines the formation of hydration products which, in turn, affect the porosity of the hardened cement paste and, as shown in Table 2-7, these pores have an influence on shrinkage of the paste. Therefore, the chemical composition of the binder should also be considered.

In order to do this, a second analysis was carried out which included the variables identified by the previous analysis, and also the major oxide contents of the binder – the calculation of which was discussed in Chapter 6.2.1 and 6.3.2. The data used in this analysis is shown in Table 6-39, with the results of the best subset regression shown in Table 6-40, and the factor loading plots shown in Figure 6-70 to Figure 6-73.

Taking into consideration the R^2 adjusted values only, it would appear that subset 2K best explains the variation of ultimate drying shrinkage. Subset 2K also has the lowest standard error, which suggests that it is also the most accurate of the models. However,

the Mallows' Cp value is relatively low in comparison to the number of parameters considered, and so the model may lack precision.

Taking the factor analysis into consideration, in all rotations, the SiO_2 content and ultimate shrinkage are shown to be the most closely correlated. In three of the four rotations, the previously identified variables 'oven-dry density' and 'maximum aggregate size' are both shown to have strong anti-correlations to ultimate shrinkage. As subset 2K includes these three factors, this is further support for the selection of 2K as the subset which best explains ultimate shrinkage. As such, the regression equation for ultimate shrinkage, with standard error of 0.009716, is:

$$US = 0.0747 + 0.00212 \times AC - 0.000090 \times ODD - 0.000736 \times MAS - 0.00445 \times Fe_2O_3 + 0.0239 \times MgO + 0.00299 \times SiO_2 \quad (51)$$

where:

Fe_2O_3 is the Fe_2O_3 content attributed to the binder, as a % by total mass of concrete;

MgO is the MgO content attributed to the binder, as a % by total mass of concrete;

SiO_2 is the SiO_2 content attributed to the binder, as a % by total mass of concrete;

Using this equation, a second prediction of ultimate was calculated for each sample and compared to the actual ultimate shrinkage observed during the experimental procedure, as shown in Table 6-41. The errors of the predicted ultimate shrinkage calculated using regression equation 1 (eq. 50) and regression equation 2 (eq. 51) are shown in Figure 6-74 and Figure 6-75, respectively. These plots, as well as the comparison of the standard error of each regression equation, show that the second model, which incorporates both physical and chemical characteristics, is both more accurate and more precise.

However, these results should be considered with caution due the potential for errors in the chemical composition data, as discussed previously in Chapter 6.3.2. Furthermore, these analyses were conducted on the results from only 23 samples. As such, additional studies on a much larger size and range of samples with known chemical composition are required to fully determine the influence of these variable on drying shrinkage, and enable the conception of a model which can make more accurate and precise predictions.

Table 6-39 – Data used in second multivariate analysis

SAMPLE	ULTIMATE SHRINKAGE	AGGREGATE CONTENT	OVEN-DRY DENSITY	MAX. AGGREGATE SIZE	Al_2O_3	CaO	Fe_2O_3	MgO	SiO_2	SO_3
	%	*%*	*kg/m3*	*mm*	*%*	*%*	*%*	*%*	*%*	*%*
03	0.045	70.9	2193	30	3.1	8.2	2.4	0.9	13.3	0.3
04	0.033	80.2	2282	45	3.5	3.9	2.2	0.9	8.0	0.1
05	0.030	67.9	2286	40	4.5	10.3	3.1	1.0	11.5	0.4
06	0.041	72.1	2147	35	4.1	7.7	2.4	0.9	11.1	0.2
08	0.035	69.4	2237	40	3.8	9.1	2.8	1.0	12.3	0.3
09	0.031	60.5	2337	25	5.0	13.7	3.3	1.1	14.2	0.4
10	0.056	64.7	2074	20	4.9	11.4	3.4	1.0	12.5	0.2
11	0.043	68.0	2118	25	5.3	14.1	3.6	1.2	5.5	0.5
12	0.036	65.3	2068	35	4.2	14.7	3.8	1.2	9.0	0.5
14	0.052	46.0	2104	25	3.9	27.8	7.2	4.0	8.6	0.8
15	0.051	74.5	2221	25	3.4	4.1	3.2	1.1	11.9	0.3
16	0.064	71.2	2089	25	3.8	7.8	5.2	1.7	9.1	0.2
17	0.073	70.4	2076	30	3.4	8.8	4.6	1.5	9.9	0.2
18	0.073	70.1	2077	30	3.9	6.6	4.2	1.6	12.2	0.2
20	0.052	74.4	2037	55	3.6	6.0	1.1	0.6	12.7	0.2
21	0.034	82.2	2372	55	2.6	4.7	1.1	0.4	8.0	0.2
37	0.085	71.0	2057	35	3.3	7.9	2.2	1.0	13.2	0.4
43	0.101	54.4	1581	14	9.2	10.9	3.4	0.9	19.2	0.8
46	0.082	84.5	1966	12	1.7	5.9	1.3	0.7	5.2	0.3
47	0.095	83.8	2103	15	2.1	5.2	1.1	0.6	6.4	0.2
48	0.077	70.2	2193	22	4.3	7.0	2.3	1.4	13.0	0.4
74	0.034	68.7	2184	20	3.3	17.7	3.7	1.3	4.2	0.9
84	0.027	76.8	2379	70	3.5	4.2	3.2	1.7	10.0	0.2

Table 6-40 – Results of second 'best subset regression' for response 'ultimate shrinkage'

Subset	Variables	R-Sq	R-Sq(adj)	C-p	S	Aggregate Content	Oven-Dry Density	Max. Aggregate	Al_2O_3	CaO	Fe_2O_3	MgO	SiO_2	SO_3
2A	1	55.6	53.5	24.0	0.015337		x							
2B	1	34.0	30.8	44.9	0.018709			x						
2C	2	64.7	61.1	17.2	0.014028		x		x					
2D	2	63.4	59.7	18.4	0.014273		x			x				
2E	3	72.8	68.5	11.3	0.012624		x	x		x				
2F	3	69.4	64.5	14.7	0.013402	x	x	x						
2G	4	80.2	75.7	6.2	0.011079		x	x		x		x		
2H	4	76.1	70.8	10.1	0.012159		x	x	x	x				
2I	5	85.3	81.0	3.2	0.009807		x	x		x	x	x		
2J	5	85.0	80.6	3.5	0.009909	x	x	x				x	x	
2K	6	86.4	81.3	4.1	0.009716	x	x	x			x	x	x	
2L	6	85.9	80.6	4.7	0.009917	x	x	x		x		x	x	
2M	7	86.5	80.2	6.1	0.010023	x	x	x	x	x		x	x	
2N	7	86.5	80.1	6.1	0.010029	x	x	x		x	x	x	x	
2O	8	86.6	78.9	8.0	0.010342	x	x	x	x	x		x	x	x
2P	8	86.5	78.8	8.0	0.010352	x	x	x	x	x	x	x	x	
2Q	9	86.6	77.3	10.0	0.010724	x	x	x	x	x	x	x	x	x

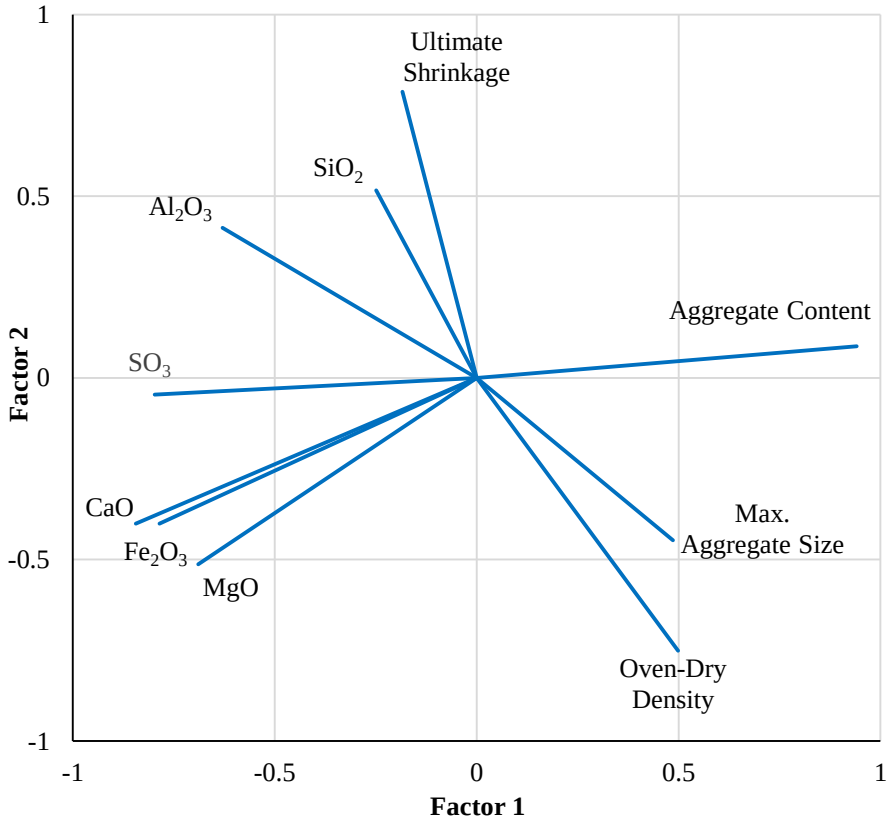

Figure 6-70 – Factor loading plot, analysis 2 (no rotation)

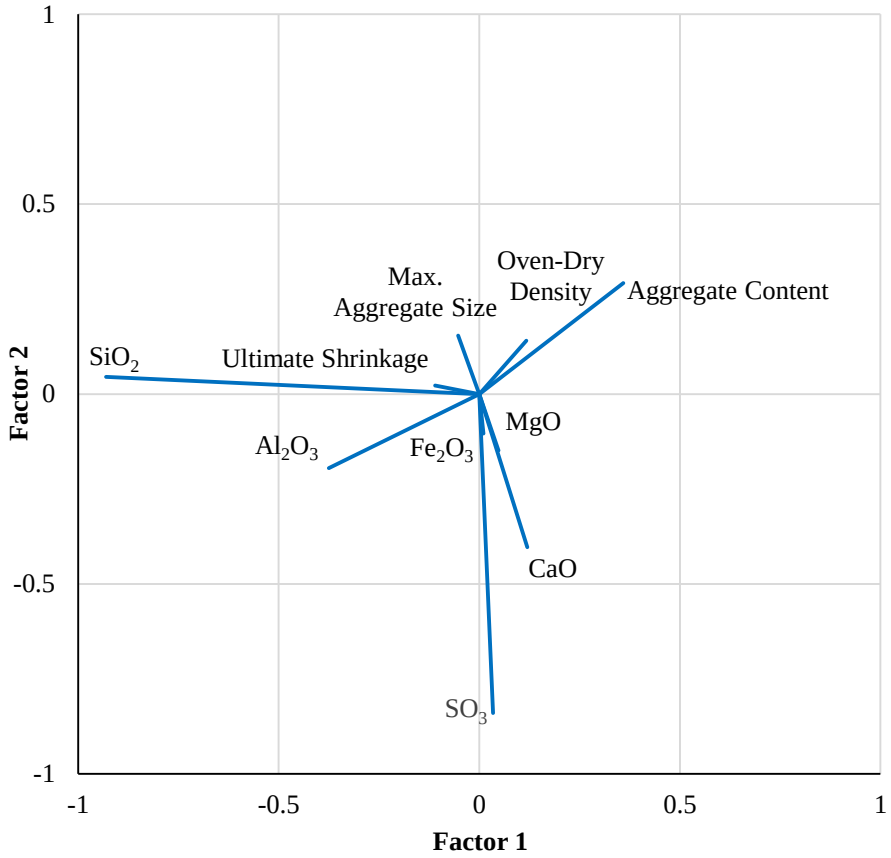

Figure 6-71 – Factor loading plot, analysis 2 (Equimax rotation)

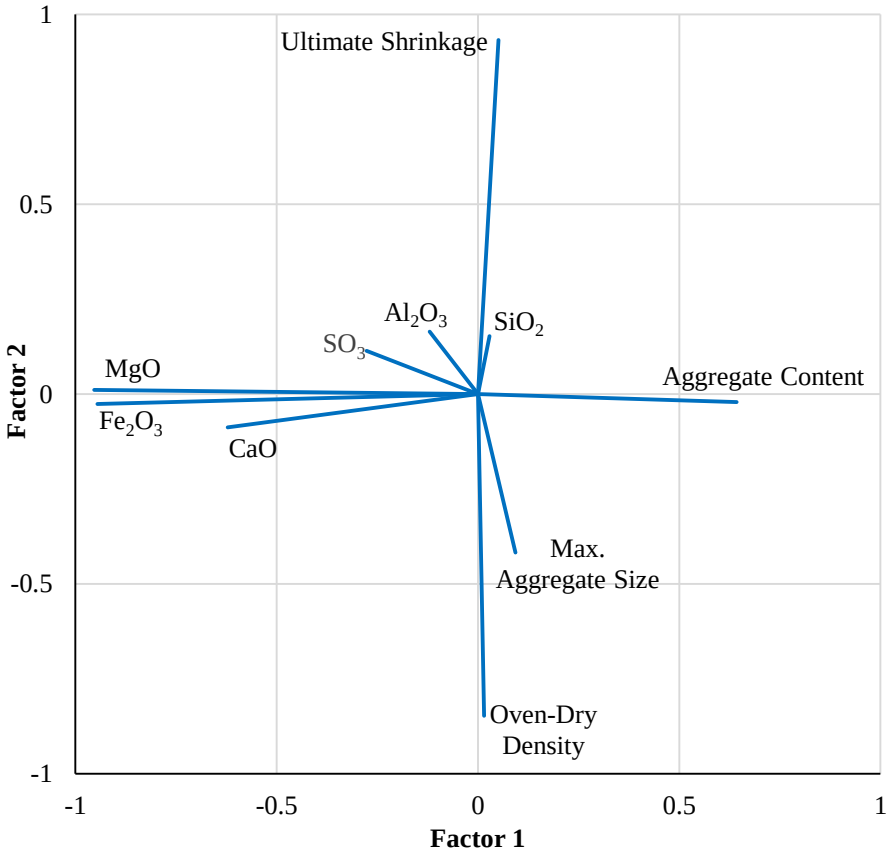

Figure 6-72 – Factor loading plot, analysis 2 (Varimax rotation)

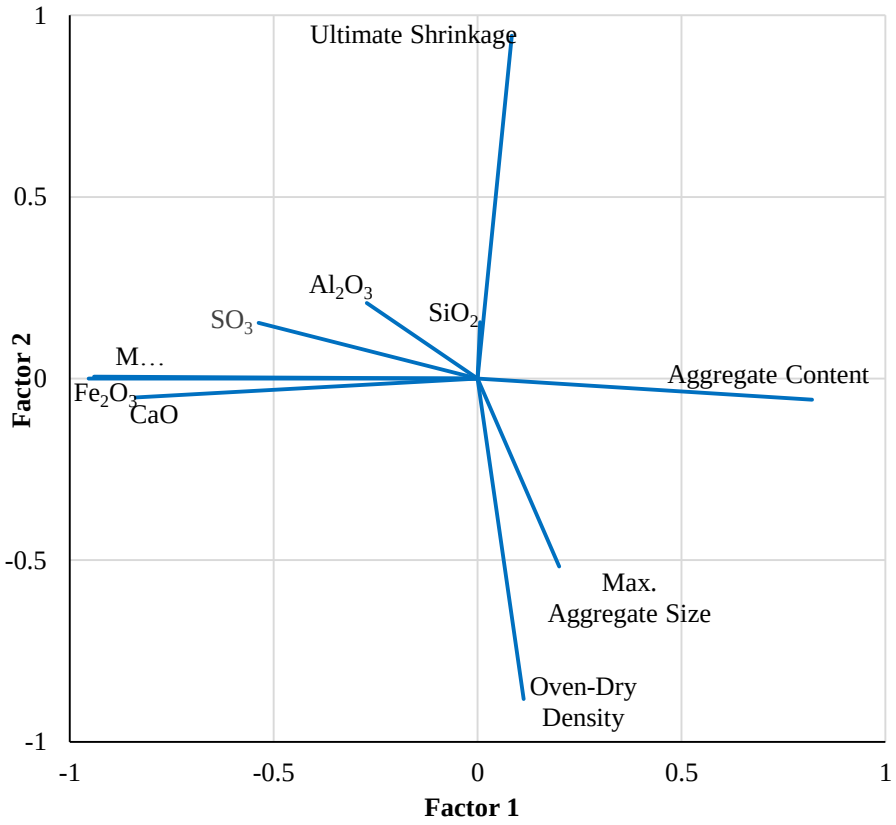

Figure 6-73 – Factor loading plot, analysis 2 (Quartimax rotation)

Table 6-41 – Comparison between actual shrinkage observed and shrinkage prediction 2

SAMPLE	ULTIMATE SHRINKAGE OBSERVED	ULIMATE SHRINKAGE PREDICTED	ERROR
3	0.045	0.056	0.011
4	0.033	0.041	0.008
5	0.030	0.029	-0.001
6	0.041	0.052	0.011
8	0.035	0.039	0.004
9	0.031	0.029	-0.002
10	0.056	0.056	0.000
11	0.043	0.039	-0.004
12	0.036	0.040	0.004
14	0.052	0.054	0.002
15	0.051	0.063	0.012
16	0.064	0.064	0.000
17	0.073	0.061	-0.012
18	0.073	0.070	-0.003
20	0.052	0.056	0.004
21	0.034	0.022	-0.012
37	0.085	0.067	-0.018
43	0.101	0.102	0.001
46	0.082	0.094	0.012
47	0.095	0.080	-0.015
48	0.077	0.071	-0.006
74	0.034	0.036	0.002
84	0.027	0.028	0.001

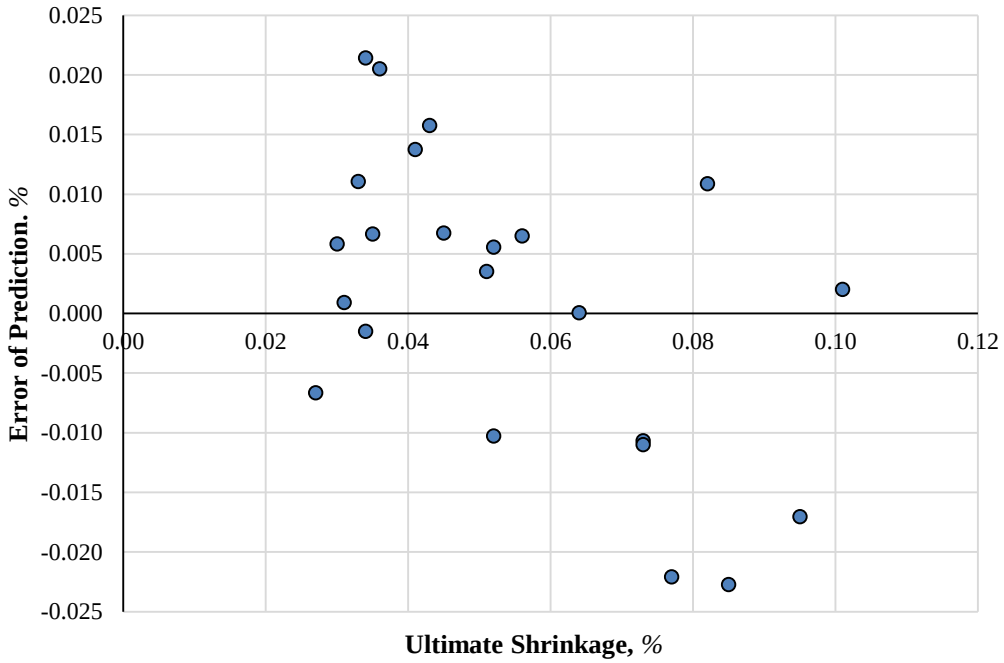

Figure 6-74 – Error of predicted shrinkage using regression equation 1 plotted against actual ultimate shrinkage observed

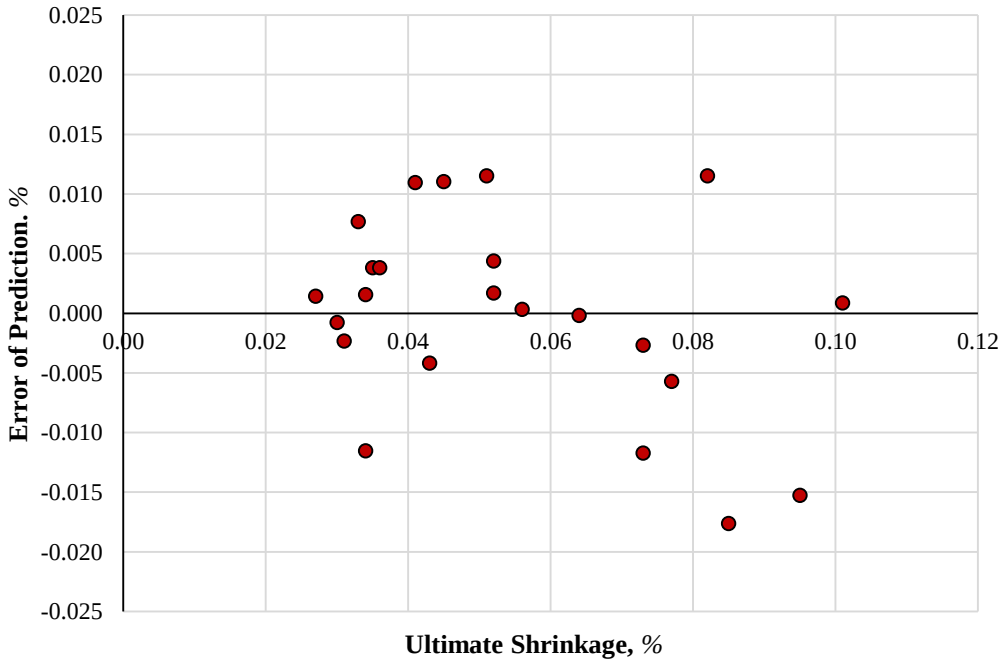

Figure 6-75 – Error of predicted shrinkage using regression equation 2 plotted against actual ultimate shrinkage observed

Variables Not Considered In Analysis

There are, however, some variables which influence drying shrinkage that were not considered in this analysis. While aggregate content, grading (FM) and maximum size were all considered, the type and shrinkage capacity of the aggregate were not. As previously discussed, the use of aggregate prone to shrinkage results in increased

shrinkage of concrete (Building Research Establishment, 1991a), and this is likely to have had an effect on the ultimate shrinkage. In particular, sample 43 – which was made using an artificial lightweight aggregate – exhibited extremely high ultimate shrinkage, and this may have been incorrectly attributed to other variables in the statistical analysis.

Finally, this analysis does not consider the effects of external restraints, such as steel reinforcement, and these will ultimately have an effect on the amount of shrinkage that the concrete would undergo if *in-situ*.

Implications for Historically-Significant Structures

The results if this study pose implications to the conservation of historically-significant structures in two regards:

The first of these is in respect to the design of drying shrinkage properties for repair materials – the importance of which was discussed in Chapter 2.6.1. The results of the statistical analysis suggest that the key variables influencing ultimate shrinkage are oven-dry density, maximum aggregate size and aggregate content, and, as a result, any purpose made like-for-like repair material would need to replicate these in order to have matching shrinkage properties.

However, as discussed in Chapter 4, there are significant challenges in accurately determining concrete properties such as density and aggregate content – the latter of which is further complicated for the reasons discussed in Chapter 6.3.1 – when there is a limited amount of original material on which to undertake analysis. Furthermore, it is clear from the second statistical analysis that the chemical composition of the binder is also a significant factor which affects drying shrinkage, and, as discussed in Chapter 6.3.2, there are still challenges in accurately determining this.

While it seems that accurately designing and manufacturing *identical* like-for-like replacements with matching shrinkage properties could be quite challenging, relationships between particular variables and ultimate drying shrinkage have been established in this study. This suggests it should be possible to formulate repair materials with appropriate shrinkage characteristics, which can also be manufactured to match the aesthetic of the original material without taking away from the historic character of a structure. However, for some conservators, there may be concern over the 'historical authenticity' of anything over than an *exact* like-for-like replacement.

The second implication of these results is in respect to climate change. In all cases, the samples reached a state of equilibrium at controlled temperature and relative humidity, where drying shrinkage did not progress any further. However, when the samples were oven-dried – resulting in severe change in temperature and relative humidity – drying shrinkage progressed further. On average, oven-drying resulted in an increase of shrinkage strain from the maximum observed after air-drying for 85 days in the controlled environment, by a factor of 2.06 (105% increase). However, it should be noted that the increase for each sample was dependent on the SA/V and volume of the samples, which affected the proportion of ultimate shrinkage which was observed after air-drying for 85 days in the controlled environment.

This presents the possibility that, as climate change occurs, the drying shrinkage cycles of concrete structures will change. While the estimates of the extent to which climate change will affect Scotland vary significantly, as shown in Figure 6-76 and Figure 6-77, it is clear that climate change is inevitable, and this may affect concrete structures in two ways.

Firstly, an increase in the drying shrinkage of existing structures could result in both the formation of new cracks and widening of existing cracks. This, in turn, increases the risk of other durability related issues which will require remedial action to be taken. Secondly, if repair materials are designed to have specific shrinkage properties based on the behaviour of original material, and these change as a result of climate changes, this could result in an increase in the failure rate of concrete repairs if the shrinkage properties of the repair material do not change similarly.

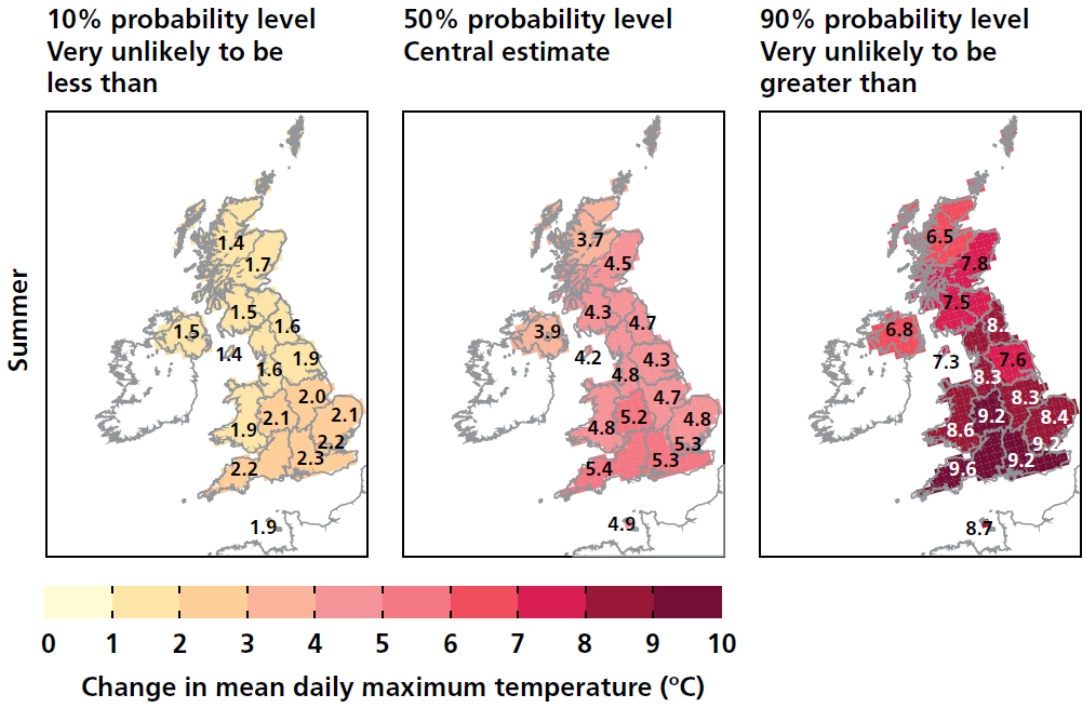

Figure 6-76 – 10, 50 and 90% probability levels of changes to mean daily maximum temperature in summer, by the 2080s, under the Medium emissions scenario (Jenkins, et al., 2009)

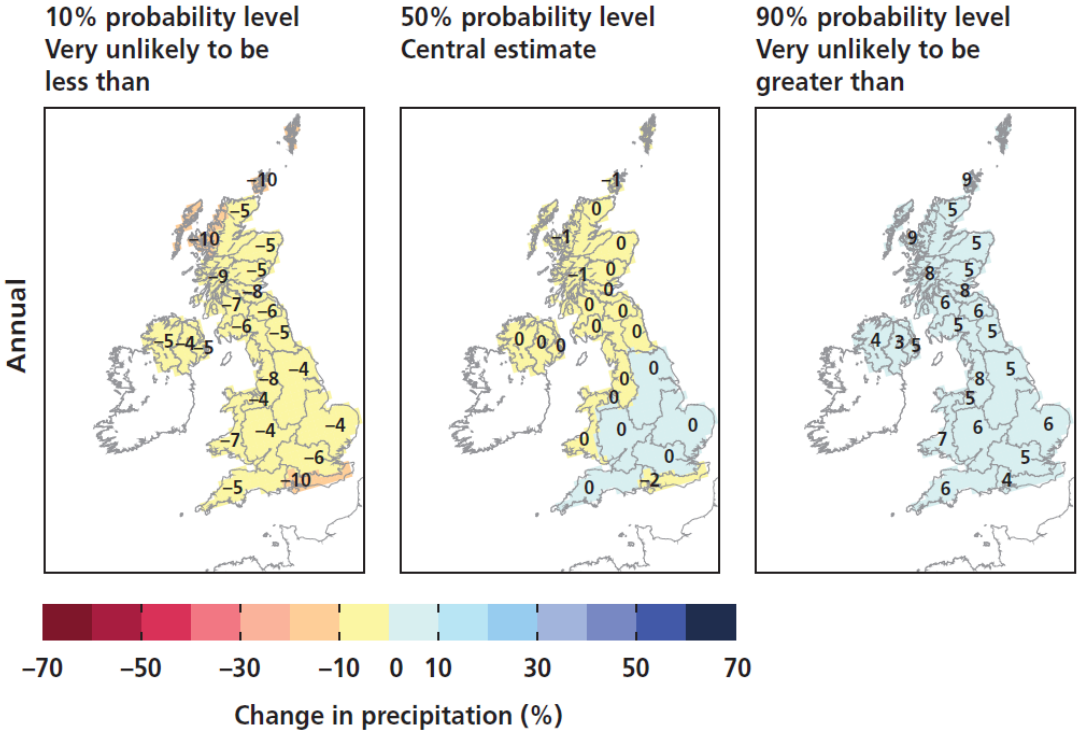

Figure 6-77 – Changes to annual mean precipitation at the 10, 50 and 90% probability levels, by the 2080s under Medium emissions, averaged over river basins (Jenkins, *et al.*, 2009)

6.4 CONCLUSIONS

The aim of this historic sample study was to analyse a wide variety of cement, mortar and concrete samples from historic structures (pre-dating 1950) across Scotland to determine the differences in Portland cement and other constituents that exist as a result of changes in manufacturing technology and processes over time, available raw materials, and the introduction of material standards and design legislation.

While the results of this study have given an insight into cement and other constituents of early concrete from structures across Scotland, the limited number of samples, and the range of material type – such as varying types of concrete which were cast *in-situ* (reinforced, mass, lightweight), precast concrete, mortar and render – limited the extent to which meaningful relationships could be identified. As such, the data gathered during this study is not a complete representation of early concrete in Scotland, but an initial foundation on which further work can expand and build upon.

One important conclusion of this historic sample study was that, at present, there is a lack of suitable techniques and standardised analysis methods which can be used to accurately determine the composition of historic concrete samples. While some reasons for this were discussed previously in Chapter 4, the historic sample study brought to light further issues related to the determination of chemical composition of binder, as well as determination of overall cement and aggregate content. Specifically, the presence of amorphous material – which was not acid-soluble – meant that it was not possible to directly analyse the chemical composition of the binder or aggregate. Instead, the chemical composition of the concrete had to be analysed by XRF and the insoluble residue from acid digestion by both XRD and XRF, and the composition of the aggregate and binder estimated from these results.

However, in order to this, it had to be assumed that 100% of the amorphous material originated from the binder, and it became clear in the analysis of the results that this was clearly not always the case. This introduced a significant risk of error, as it affected not only the results obtained from XRF and XRD, but also the calculated binder and aggregate contents. As such, it can be concluded that new techniques and standardised test procedures are required for the accurate analyses of historic concrete samples.

The results of the drying shrinkage study suggest that the key variables influencing ultimate shrinkage are oven-dry density, maximum aggregate size and aggregate content,

with the chemical composition of the binder also having a significant influence. A model taking these variables into consideration was formulated, but further research is required to expand on this and produce a model which can more accurately predict the shrinkage of the repair material. While a predictive model should allow repair materials with appropriate shrinkage characteristics to be formulated, there are concerns about how accurately the variables from the original material can be determined using current methods.

As previously stated, given the effects of other factors, such as curing conditions and the degree of hydration, on the microstructure and mechanical properties of hardened concrete it may, in reality, be more effective to undertake a more in-depth study of the *in-situ* material, and to try and replicate its physical properties as closely as possible through a series of trials. For example, DEMEC studs like the ones used in this study could easily be applied to strategic positions on a structure *in-situ*, and the strain measured over the course of a year to take into account the key variations that occur as a result of the change in environmental conditions. The data obtained would allow a shrinkage profile of the material to be developed, which would inform conservators on the range of shrinkage parameters which need to be met by a repair material.

Furthermore, as discussed in Chapter 6.3.5.1, the issue of climate change is one which needs to be considered in relation to the conservation of historically-significant concrete structures and the use of repair materials. As changes in temperature and precipitation levels occur, it is possible that the drying shrinkage cycles of concrete structures will alter in response to these and may result in both the formation of new cracks and widening of existing cracks. As such, the need for concrete repairs may increase with climate change and any repair materials which are designed with drying shrinkage in mind will also need to respond accordingly.

7 CONCLUSION

7.1 SUMMARY OF CHAPTER CONCLUSIONS

7.1.1 Chapter 4: Control Study

In the control study, standard techniques were applied in the analysis of hardened concrete samples, which had been prepared in the laboratory with known mix proportions, in order to determine their accuracy and usefulness in assessing historic concrete samples.

It became clear from the results of these tests that, while these standard techniques are adequate for assessing quality control of concrete manufacturing, they cannot be used to accurately determine the w/c ratio or the original mix proportions of historic concrete due to the physical and chemical changes which have occurred. Furthermore, errors in analyses increase significantly as the size of the sample decreases, which presents further complications as access to concrete samples from historically-significant structures can be very limited.

While the current approach to the repair of historic concrete structures is to use purpose made 'like-for-like' replacements, it is, at present, not possible to guarantee the accurate analysis of the material which is to be replaced.

7.1.2 Chapter 5: Review of Historic Test Data

Pre-existing test data was reviewed in order to identify trends in the design and construction of early concrete structures in Scotland. During this review, it became clear that many early concrete structures are inadequately designed for durability given their state of exposure. As such, it is likely that these structures are at significant risk of deterioration from freeze-thaw attack as well as both carbonation and chloride induced corrosion

7.1.3 Chapter 6: Historic Sample Study

During the historic sample study, it became clear that there are further issues with current analysis techniques to those discussed in Chapter 4, and, as such, it is unlikely that like-for-like repairs can be produced with sufficient accuracy using current methods. These issues predominantly relate to the presence of amorphous material in the hardened concrete and the inability to accurately attribute it to either the binder or aggregate during chemical analysis.

In addition to analyses of the chemical composition of the concrete samples, a study of the drying shrinkage properties of 24 of the samples was undertaken and a statistical analysis of the results performed in order to determine which physical properties had the most influence on drying shrinkage. The results suggested that, of the properties included in the analysis, the most important variables affecting ultimate shrinkage were oven-dry density, maximum aggregate size and aggregate content.

7.2 IMPLICATIONS OF RESEARCH

The current approach to the conservation of historically-significant concrete is to carry out repairs with 'like-for-like' replacement materials, as this will, in theory, provide a repair which has suitable mechanical and chemical properties, while preserving the historic character of the structure.

However, over the course of this project, it has become clear that this approach is flawed as there is, at present, a lack of suitable techniques which can be used to accurately determine the composition of the original material – making it difficult to guarantee an *exact* like-for-like replacement.

The American Concrete Institute (1999) defines the following five processes which are applicable in the conservation of concrete structures:

Table 7-1 – Definitions of terms applicable to the conservation of concrete structures

TERM	DEFINITION
Preservation	The process of maintaining a structure in its present condition and arresting further deterioration
Rehabilitation	The process of repairing or modifying a structure to a desired useful condition
Repair	To replace or correct deteriorated, damaged or faulty materials, components, or elements of a structure
Restoration	The process of re-establishing the materials, form, and appearance of a structure to those of a particular era of the structure
Strengthening	The process of increasing the load-resistance capacity of a structure or portion thereof

Source: Original definitions from ACI 364.1 R-94 (American Concrete Institute, 1999)

However, each of these processes represent a different priority and, therefore, a different approach to the conservation of historically-significant structures, and each one is not necessarily compatible with other approaches.

With this in mind, if the conservation of historically-significant concrete structures – and historically-significant structures in general – is to be successful, the primary focus of the heritage community has to be on determining the correct philosophical approach in each particular scenario. It is only once this has been determined that the relevant engineering solution can be applied. Unfortunately, it is inevitable that there will have to be compromise between the need for structural integrity and the desire to retain historic character.

7.3 RECOMMENDATIONS FOR FUTURE WORK

The main conclusion that can be drawn from this project is that current methods for the forensic analysis historic concrete are inadequate, and so further work is required in following three areas:

1. New techniques and standardised analysis methods

At present, there exists a lack of standardised methods for the analysis of concrete which is chemically or physically damaged – as that which comes from historic structures usually is – and, as a result, analyses are often carried out following standard procedures which are unsuitable and give misleading results.

Furthermore, as material from historically-significant structures is difficult to obtain, these analyses are being carried out on samples which are far smaller than the required

minimum sample size. This is problematic as there can be a great deal of variability between small samples taken from different parts of a single mass due to a variety of physical phenomena, and this means that the samples taken may not be representative of the overall concrete, or a separate, specific area of which a greater understanding is desired.

It is essential that conservators appreciate the limitations of current techniques and that the heritage community acknowledges the need for both new analysis techniques and appropriate standardisation of existing analysis methods. This need not only applies to historic concrete, but to other historic materials as well – such as mortar and other cementitious materials – as has been raised by other researchers (Goins, 2004; Hughes, *et al*., 2016).

2. Alternative repair materials and their compatibility

At present, it is not possible to guarantee the accurate forensic analysis of the material which is to be replaced, and current proprietary repair materials are unsuitable for use with historic concrete. However, given the effects of other factors, such as curing conditions and the degree of hydration, on the microstructure and mechanical properties of hardened concrete it may, in reality, not be possible to ever create a completely identical like-for-like repair material.

While the authenticity of repair materials is important to the heritage community from the perspective of retaining the historic character of a structure, there will, inevitably, be cases where there is a legal obligation to maintain the structural integrity of historic sites which must take precedent. As such, the heritage community needs to be open to the idea of new repair materials, and research has to be undertaken in order to develop them.

While the issue of compatibility of repair mortars for masonry in a conservation context is one which has been the focus of many authors (Groot, 2004; Van Balen, et al., 2005; Cizer, et al., 2010; Torney, et al., 2014), and the compatibility issues relating to concrete repair materials more generally has been shown to be well understood (Morgan, 1996; Decter & Keeley, 1997), it seems that very little work has been done in the field of compatible repair materials for concrete structures of historical value. As such, this an area in which particular attention is required. In particular, a standard compatibility model – such as that proposed by (Rodrigues & Grossi, 2007) – that could be applied to concrete repairs would be of great benefit to the built heritage conservation community.

3. Methods of protection and prevention of concrete deterioration

The repair of historically-significant structures should always be a last resort. This view is reflected in the manifesto of the Society for the Protection of Ancient Buildings (SPAB, 2017) which states:

> *It is for all these buildings, therefore, of all times and styles, that we plead, and call upon those who have to deal with them, to put Protection in the place of Restoration, to stave off decay by daily care…*

At present, there exists a wide variety of methods for protecting concrete and preventing the degradation of steel reinforcement – some of which were discussed Chapter 2.5 – and, if implemented correctly, the use of these can prevent the need for more invasive repairs in the future.

For example, cathodic protection can be installed in discreet locations to protect the steel in reinforced concrete structures, carbonated concrete can undergo re-alkalisations to restore the protective passive alkaline environment, and deleterious chlorides which have ingressed can be extracted from concrete. There are also a variety of barrier and impregnation systems available – such as coatings, blockers and sealants – some of which may be suitable in certain circumstances, depending on the effects that they will have on the surface characteristics and aesthetics of a structure.

However, conservators need to have a thorough understanding of the mechanisms by which these work to ensure the correct solutions are applied, and every effort made to ensure they are implemented with minimal intrusion. If this can be achieved, then Scotland's significant heritage of early concrete structures can be preserved for generations to come.

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